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Development of a Portable Device to Collect Sulfuric Acid Aerosol

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DEVELOPMENT OF A PORTABLE DEVICE TO COLLECT SULFURIC ACID AEROSOL Interim Report



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PREFACE

The Environmental Protection Agency has a need for a better method than is presently available to determine concentrations of sulfuric acid in the ambient atmosphere. This need exists because of the recognition of the potentially harmful health effects of sulfuric acid and sulfates generated by burning increased amounts of coal and particularly by the use of catalytic converters in automobiles.

In research on this analytical problem under this contract and other closely related contracts emphasis has been placed on the use of a Teflon filter as a sampling device and the ultimate use of a sulfur-specific flame photometric detector for measuring the sulfur evolved on heating the filter. This contract was concerned primarily with sampling aspects of the overall method. The principal task was an investigation of the possible interfering effects of other gaseous and particulate atmospheric pollutants, on the collection of sulfuric acid on a filter. Although several kinds of analytical procedures, including the flame photometric technique, were used in this investigation to measure sulfuric acid, the study did not encompass all details of a complete sampling and analytical method; instead, it was limited to the evaluation of a filter as a sampling device, especially to studies of interactions between collected sulfuric acid aerosol particles and other simultaneously occurring pollutants.

ABSTRACT

The purpose of this investigation was to determine the effects of possible atmospheric interferents on the quantitative collection of sulfuric acid aerosol on a filter.

Sulfuric acid aerosol was generated in the laboratory with a flame atomizer and collected on Teflon filters. The filters were exposed to potential gas and vapor interferents and to particulate interferents during, before, or after the collection of the sulfuric acid.

Measurements of sulfuric acid were made by an acid-base indicator method or by extraction with benzaldehyde and titration. Also, sulfur evolved on heating the filters was measured by the flame photometric method.

Ammonia, particulate calcium carbonate, and ambient particulate material (collected near a busy street) caused severe losses of sulfuric acid; particulate ferric oxide and silicate clay caused an intermediate loss; pyridine and phenol vapors, particulate fly ash, and soot caused little or no loss; and sulfur dioxide and nitrogen dioxide had no effect (in the absence of other materials).

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SECTION 1

INTRODUCTION

The increasing use of sulfur-bearing coal for the production of electrical energy, the generation of significant quantities of sulfuric acid aerosol by catalytic converters in automobiles, and the appearance of new information on the irritant effects of sulfuric acid and sulfates, are factors that have combined to intensify interest in the measurement of ambient sulfuric acid aerosol. The emission of sulfuric acid by automobiles is a problem of special interest because of the fairly high concentrations found in the immediate vicinity of roadways and the small size of the sulfuric acid particles generated.

The potentially harmful health effects stem from certain unique properties of sulfuric acid aerosol. Sulfuric acid is the most severe bronchial and lung irritant among the various species of sulfur compounds that can occur in the atmosphere. The particles derived from automobiles have a mass mean diameter of only a few hundredths of a micrometer and therefore can penetrate deeply into the lung and be deposited in the alveoli. These small particles are relatively highly concentrated in terms of the normality of the sulfuric acid and are therefore stronger irritants than particles that have grown in size over a period of time by coagulation and absorption of water vapor.

In order to assess the health effects potential of sulfuric acid under these circumstances, it is necessary to have sampling and analytical methods that will measure sulfuric acid concentrations without interference or artifacts arising from the presence of other substances in the sampled atmosphere or from various environmental factors such as relative humidity or temperature. Because many interfering reactions are possible, especially during the collection of a sample, the accurate determination of sulfuric acid aerosol is a difficult problem that has so far not been adequately solved.

Although sampling cannot be arbitrarily isolated from the method of analysis subsequently used to determine the species sought, there are certain difficulties peculiar to sampling sulfuric acid aerosol. In general terms, these difficulties may be said to result from interactions of sulfuric acid with other particulate and gaseous constituents of the ambient atmosphere or the sample and from the simultaneous presence in the atmosphere

of sulfate salts and sulfur dioxide. Reactions of sulfuric acid with copollutants have been shown to occur on filters, the collection medium that is generally best suited for sampling atmospheric particulate material. The oxidation of sulfur dioxide to sulfate also occurs on filters under certain conditions. These phenomena—and others that may be expected to occur—often result in failure of attempts to measure ambient concentrations of sulfuric acid because some or all of the acid is lost during the sampling process. Furthermore, methods of analysis that involve dissolving the sulfuric acid along with other soluble constituents of the sample introduce errors resulting from reactions that occur in the solvent medium; a sampling method that will permit subsequent processing and analysis of the sample without loss (or addition) of sulfuric acid is therefore desirable.

Work on this contract has been concerned principally with analytical evaluation of possible interfering effects that may occur during collection of a sample on a filter. During the early months of the contract period efforts were made to establish techniques that would permit studies to be conducted with a submicron aerosol of sulfuric acid at a concentration ($10 \mu\text{g}/\text{m}^3$) near reported ambient levels. In accordance with the Scope of Work, it was intended that interference studies would be conducted by introducing the potential particulate and gaseous interferences directly into the aerosol, with subsequent collection of a sample and analysis. However, inability to obtain a clean aerosol free of significant levels of background ammonia and amines, nitrogen dioxide, and particulate material finally led to the abandonment of this approach. Instead, an aerosol with a concentration of about $300 \mu\text{g}/\text{m}^3$ was used. At this concentration level, the ratio of sulfuric acid generated to the volume of dilution air used is such that the relative amounts of background interferences are reduced to less significant levels. Instead of mixing the interferent materials to be studied directly into the aerosol, 30- to 50- μg amounts of sulfuric acid were deposited on a filter in 10 to 20 min and the interferent gas or particulate material was then passed through or deposited on the filter. In some instances, particulate interferences were added to the filter prior to the collection of sulfuric acid.

This report describes the techniques used to generate the sulfuric acid aerosol; the analytical methods used to measure sulfuric acid, total sulfate, and several interferent materials; and the apparatus and procedures used in studies of the flame photometric detection of sulfur evolved from heated filters. It gives the results of experiments designed to determine the effects of various potential interferences on the collection of sulfuric acid on filters, and summarizes the conclusions reached.

SECTION 2

CONCLUSIONS AND SUMMARY OF RESULTS

The collection of sulfuric acid aerosol on Teflon filters, as a first step in the measurement of ambient sulfuric acid concentrations, is subject to interference by alkaline gases and by particulate materials in the sample air. Strong interference is caused by gaseous ammonia, particulate calcium carbonate, and ambient particulate material from an urban environment; an intermediate degree of interference is caused by ferric oxide and a silicate clay soil; and relatively little or no interference is caused by nitrogen dioxide, sulfur dioxide, fly ash, soot, and the vapors of pyridine and phenol. In the presence of ambient particulate material sulfuric acid or sulfate appears to be reduced slowly to sulfur dioxide when heated on a Teflon filter. These conclusions are based on the experimental evidence summarized in the following paragraphs. This evidence suggests that the determination of atmospheric sulfuric acid by collection of a sample on a filter over a period of time is subject to error from interfering reactions that may occur during sampling.

RESULTS OF EXPERIMENTS USING THE BROMOPHENOL BLUE METHOD OF DETERMINING TOTAL ACID

- Mitex filters on which 50 μ g of sulfuric acid had been deposited as a single drop of standard solution were exposed to ambient air in an industrial area at 15 l/min for 10, 30, or 60 min. No losses of sulfuric acid were observed in 10 or 30 min, but in 60 min about 25% of the acid was neutralized, as measured by the bromophenol blue method.
- In the absence of other contaminants, sulfur dioxide added directly to sulfuric acid in the aerosol phase did not affect the amount of acid collected on a Mitex filter, as measured by the bromophenol blue method, or the amount of total sulfate, as determined by the barium chloranilate method.
- In the absence of other contaminants, nitrogen dioxide added directly to the sulfuric acid aerosol had no effect on the amount of acid or total sulfate on a Mitex filter, as measured by the bromophenol blue and barium chloranilate methods.

- When a Mitex filter that had been preloaded with 0.45 μmol of sulfuric acid from the aerosol generator was exposed to a known amount (0.14 μmol) of ammonia in air, approximately 0.1 μmol of the sulfuric acid disappeared, as measured by the bromophenol blue method.
- Mitex filters upon which various amounts of sulfuric acid (20 to 80 μg) had been predeposited were exposed to an aerosol of finely divided ferric oxide. The average recovery of sulfuric acid was about 75% by the bromophenol blue method and the average recovery of total sulfate was about 95% by the barium chloranilate method.
- Mitex filters upon which 40 to 70 μg of sulfuric acid had been predeposited were exposed to an aerosol of finely divided calcium carbonate. No acid or soluble sulfate was recovered from these filters on analysis by the bromophenol blue and barium chloranilate methods. The sulfuric acid appeared to be completely converted to calcium sulfate.
- Mitex filters were exposed first to laboratory ambient particulate material and then to sulfuric acid aerosol. Upon analysis by the bromophenol blue and barium chloranilate methods, about 50% of sulfuric acid was recovered, while all of the total sulfate was recovered. Some neutralization of the sulfuric acid yielding a soluble sulfate appeared to have occurred.

RESULTS OF EXPERIMENTS USING THE BENZALDEHYDE EXTRACTION METHOD OF DETERMINING SULFURIC ACID

- The benzaldehyde extraction method was confirmed as specific for sulfuric acid in the presence of ammonium bisulfate, ammonium sulfate, and calcium sulfate. Sulfuric acid was extracted from filters with dry, freshly distilled benzaldehyde, then extracted from the organic solvent with water, and finally measured with a microadaptation of the barium-Thorin titration method.
- Measured amounts (35 to 50 μg) of sulfuric acid were deposited on Mitex filters from the aerosol and the filters were then exposed to measured quantities of ammonia (2 to 40 μg) in air. The filters were analyzed for sulfuric acid and ammonium ion and the gas passing through the filters was analyzed for unabsorbed ammonia. The results of these measurements showed that when sulfuric acid was stoichiometrically in excess, all of the ammonia was collected on the filter and the excess acid was measurable as H_2SO_4 ; when ammonia was stoichiometrically in excess, all of the sulfuric acid was neutralized and the excess ammonia was found in the effluent gas passing through the filter.

- The experiments with calcium carbonate and ferric oxide in which the sulfuric acid was determined by the bromophenol blue method were repeated with analysis by the benzaldehyde extraction method. Whether the sulfuric acid was deposited on the filter before or after the collection of calcium carbonate aerosol, losses of sulfuric acid generally in excess of 75% were observed. When filters containing pre-deposited iron oxide aerosol were exposed to sulfuric acid, approximately 95% of the sulfuric acid was recovered.
- Similar experiments were conducted with one sample of fly ash from a coal-burning electric power plant and one sample of soot deposited from a fuel-rich acetylene-air flame. No evidence of loss of significant amounts of sulfuric acid was observed with either material.
- Samples of predeposited ambient particulate material collected on Mitex filters near a busy street were exposed to sulfuric acid aerosol. Analyses of the filters by the benzaldehyde extraction method indicated that only 30 to 40% of the sulfuric acid could be recovered.
- Efforts to conduct similar experiments with predeposited calcium silicate were not successful, apparently because the strong alkalinity of the calcium silicate interfered with the analysis by the benzaldehyde extraction method. However, experiments with a clay soil containing silicates were successful and indicated that slightly more than 50% of the added sulfuric acid was recovered.
- Measured amounts of vapor of the organic amine pyridine were exposed to filters preloaded with known amounts of sulfuric acid collected from the aerosol phase as in the experiments with ammonia. However, analyses of the filters showed no significant losses of sulfuric acid with pyridine as opposed to the stoichiometric losses observed with ammonia.
- Analyses following exposures of collected sulfuric acid to measured amounts of phenol vapor also showed no significant losses of the acid.

RESULTS OF EXPERIMENTS INVOLVING FLAME PHOTOMETRIC DETECTION OF SULFUR EVOLVED FROM HEATED MITEX FILTERS

- A Meloy Sulfur Gas Analyzer was modified for these experiments, principally by connecting the detector to a glass tube in an aluminum block in which Mitex filter disks could be heated in a controlled manner so that volatilized materials could be flushed with a stream of air into the flame. The response of the detector was calibrated with

known amounts (1 to 3 μg) of sulfuric acid deposited on filters and evaporated in the heated block.

- When sulfuric acid aerosol was collected on filters containing predeposited ambient particulate material and determined by heating the filter at 200°C, the observed flame photometric detector response was much less than the response to the same amount (2 μg) of sulfuric acid alone. Moreover, the smaller initial and immediate peak response characteristic of sulfuric acid was followed by a gradually increasing response over a period of about 1 min. and then a slowly decreasing response over 5 to 10 min. These results suggested that the reduced initial response may have resulted from loss of sulfuric acid by reaction with constituents of the ambient particulate material, and that the slowly decreasing response may have resulted from reduction of sulfate to sulfur dioxide.
- Similar experiments conducted at 150°C instead of 200°C gave results that were similar, except that the responses were further attenuated because sulfuric acid was volatilized from the filters more slowly.
- At each temperature, the ambient particulate material alone (without any added sulfuric acid) gave only a small initial response, suggesting the presence of a small amount of ambient sulfuric acid. At 200°C, this small initial response was followed by the same type of gradually increasing and decreasing response observed when sulfuric acid was added, again suggesting the reduction of sulfate to sulfur dioxide by constituents of the ambient particulate material. At 150°C, the initial peak was smaller and the gradually increasing and decreasing response was not evident.
- Similar experiments conducted with predeposited calcium carbonate aerosol gave the same results that were found with the bromophenol blue and benzaldehyde extraction methods of analysis; that is, the sulfuric acid was apparently completely neutralized and no sulfur flame photometric detector response was observed. The absence of any slow response in this instance presumably resulted from the absence of any substance that could reduce sulfate to sulfur dioxide at 200°C.

SECTION 3

RECOMMENDATIONS

The results of the experimental work described in this report indicate that intensified effort should be directed toward fixation of sulfuric acid by an appropriate reaction in the aerosol phase or in or on the collection medium. Such a reaction should produce a derivative in an amount directly proportional to the amount of sulfuric acid in the air sample. The derivative itself should be measurable by a suitable analytical method without interference from other constituents of the air sample. Research is already underway elsewhere with this objective. The conclusions and results given in the previous section suggest that that research should be continued and expanded.

The Environmental Protection Agency is currently supporting the development of a sulfuric acid analyzer based on the collection of sample on a filter followed by volatilization and measurement with a flame photometric detector. This principle has certain strong potential advantages over other methods, particularly in sensitivity; however, the results of the present study show that flame photometric measurement of the sulfur volatilized from a particulate sample collected on a filter may not yield a response proportional to the ambient concentration of sulfuric acid. Further studies should be conducted to optimize this technique and, especially, to adapt it to the measurement of a derivative formed by a suitable fixation reaction.

In any further research of the type described in this report particular attention should be given to the following experimental tasks:

- Determine whether sulfuric acid aerosol generator systems other than the burner-aspirator used in this work—for example, ultrasonic generators—can be used to produce a clean aerosol free of background contaminants while maintaining the desired small particle size and allowing convenient and accurate introduction of potential interferents directly into the aerosol.

- Conduct a systematic evaluation of filter materials from which sulfuric acid (or another sulfur compound) can be volatilized for flame photometric detection.
- Investigate in depth the possible interference of sulfur dioxide and other sulfur compounds in the presence of complex ambient particulate material when the volatilization-flame photometric method is to be used for detection.
- Optimize the conditions and equipment for volatilization-flame photometric detection, especially the effects of temperature, rate of heating, and types of surfaces exposed; identify and quantitate the sulfur species evolved on heating.

SECTION 4

EXPERIMENTAL APPARATUS AND PROCEDURES

SULFURIC ACID AEROSOL GENERATOR

Construction and Operating Parameters

A generator of sulfuric acid aerosol similar to the one described by Thomas *et al.* was constructed.¹ This system was selected because it was reported to have certain attributes that were considered to be desirable for the purposes of this project. In particular, no other generator system could be expected to produce predominantly submicron particles, while simultaneously permitting flexibility for the addition of potential gaseous and particulate interferents directly to the aerosol. It also allowed easy adjustment of concentrations, flow rates, and other parameters. Furthermore, it was reported to generate no sulfur dioxide. Several problems, however, were encountered, and a substantial amount of effort was devoted to attempts to correct these difficulties.

The generator is illustrated in Figure 1. Its principal component was a Beckman No. 4020 atomizer-burner situated at the base of a 1.22-m by 99-mm i.d. Pyrex chimney. The fuel gas was hydrogen and the oxidizer was a mixture of oxygen and argon. A dilute solution of sulfuric acid was aspirated into the flame from a beaker placed underneath the burner. Filtered air was fed into a metal box placed under the bottom of the chimney and enclosing the burner. This air was forced into the box by a vacuum cleaner type blower so that excess filtered air shrouded the burner and bottom end of the chimney. The ends of two 13-mm i.d. glass probes were located close together about 10 cm below the top of the chimney. One of these probes had a side arm closed with a silicone septum through which gases could be added at known flow rates. The probes were connected to stainless steel holders for 47-mm filters, which were followed by 6-l/min critical orifices and a small Gast pump. One side of this dual sampling system was always used as the reference for determination of the concentration of the sulfuric acid aerosol, while the other side was used for the introduction of interferent gases or for holding a filter containing predeposited particulate material. The excess aerosol from the top of the chimney was exhausted through a hood.

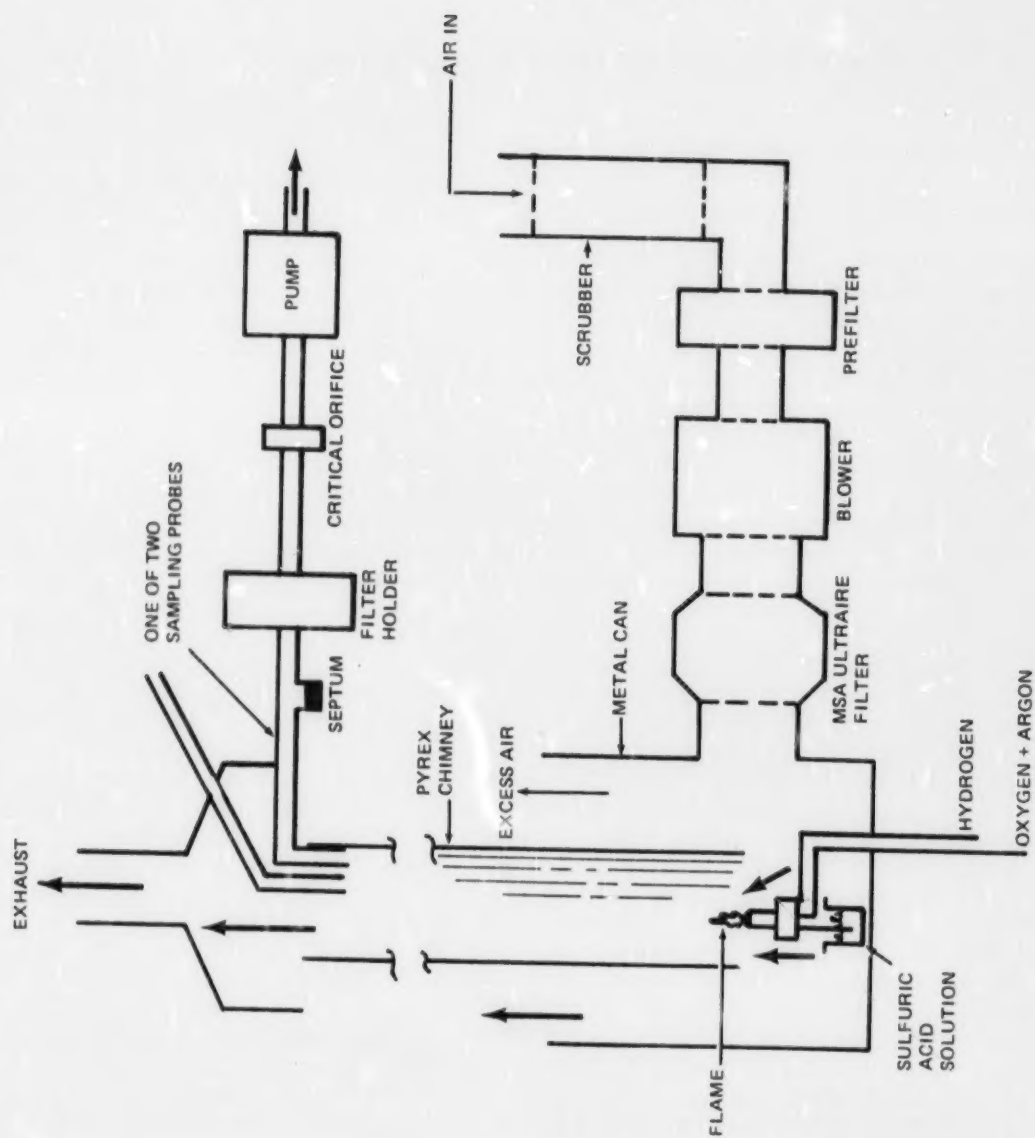


Figure 1. Sulfuric Acid Aerosol Generator (not to scale)

The principal operating parameters for the aerosol generator and their usual values were as follows:

- Hydrogen fuel gas: 15 mmHg (positive pressure)
- Oxygen-argon mixture: O₂, 105 mmHg; Ar, 672 mmHg
- Sulfuric acid solution concentration: 0.002 N
- Sulfuric acid aspiration rate: 2 ml/min
- Temperature at inlet of probe: 35°C
- Temperature at filter: 30°C
- Sampling flow rate: 6 l/min

All of these parameters were varied experimentally in order to find the optimum set of conditions.

Particle Size

An estimate of the particle-size distribution of the aerosol is given in Table 1. The conditions existing at the time these measurements were made were not identical to those given above, but the results are believed to be representative. Measurements were made with a Thermo-Systems Electrical Aerosol Size Analyzer (Model 3030) and with a modified Climet Particle Analyzer. Samples were taken at a position in the sampling system that corresponded to the position of the filter holder. Samples were also taken after the filter holder with Mitex LS filters in place, and at several positions in the metal box at the base of the chimney.

The majority of particles at a position near the location of the filter holder were found to be in the size range of 0.3 to 0.005 μ m; 98% of the mass of the particles was in this range. Slippage of the small particles through Mitex LS filters was about 3% while slippage of particles larger than 0.25 μ m was determined to be less than 0.1%. The filtered air entering the metal box was found to contain about 8.4×10^3 particles/m³ that were greater than 0.25 μ m; this was less than 0.1% of the concentration of particles in this size range found in the effluent of the generator. The dilution air also contained negligible concentrations in the size range below 0.25 μ m.

Flame Temperature

Initially, when the aerosol generator was operated under the conditions described by Thomas *et al.*, little or no sulfuric acid was found on Mitex LS filters in the sampling line. Much larger quantities were found in Greenburg-Smith backup impingers containing 80% isopropanol. This observation indicated that most of the

TABLE 1. SIZE OF SULFURIC ACID AEROSOL PARTICLES

Thermo-Systems Electrical Aerosol Size Analyzer	Size range, μm	
	1 to 0.3	0.3 to 0.005
Number of particles/ m^3	1.2×10^7	$>1.2 \times 10^{14}$
Volume, cm^3/m^3	6.6×10^{-7}	$>2.7 \times 10^{-5}$
Mass, $\mu\text{g}/\text{m}^3$ ^a	1.1	>45
Volume fraction	0.02	>0.98
Slippage through Mitex LS filter, number of particles/ m^3	—	3.3×10^{12}

Climet Particle Analyzer	Size	No. of Particles/ m^3
	Range, μm	
	>1.27	8.5×10^2
	>0.77	2.9×10^5
	>0.25	1.3×10^7
Slippage through Mitex LS filter, number of parti- cles/ m^3	0.25 μm	8.5×10^2

^aThe density of the aerosol particles was assumed to be $1.66 \text{ g}/\text{cm}^3$ (74% H_2SO_4).

sulfuric acid was in the form of vapor and that the temperature of the gas at the filter was too high. By reducing the pressure of the hydrogen fuel from the recommended value of 52 mmHg to 15 mmHg and that of oxygen from 646 mmHg to 517 mmHg, the temperature at the inlet of the probe was reduced from 200°C to about 80°C. With these conditions, and with the aspiration of 0.002 N sulfuric acid at 0.8 ml/min, quantities of sulfuric acid appropriate for analysis were collected on filters from an aerosol of 40 to 50 $\mu\text{g}/\text{m}^3$ in 2 to 3 hr with a sampling flow rate of 10 to 15 l/min.

Later, when experiments involving the addition of nitrogen dioxide to the aerosol were undertaken, it was found that the generator system produced nitrogen dioxide concentrations of 1 to 2 mg/m^3 (0.5 to 1 parts per million) at the point where the filter was located in the sampling line. It was felt that this concentration level was much too high for the types of interference experiments planned. Therefore, the composition of the burner gases was further modified to reduce the flame temperature by mixing a relatively large proportion of argon with the oxygen. With a hydrogen pressure of 15 mmHg, an oxygen pressure of 105 mmHg, and an argon pressure of 672 mmHg, the temperature of the gases at the probe inlet was reduced to about 35°C and the concentration of nitrogen dioxide at the filter was reduced to about 0.7 mg/m^3 (0.04 parts per million).

Background Contamination

In an effort to circumvent problems arising from the presence of sulfate particulate and alkaline gases in the dilution air, the generator was further modified to filter the air that entered the metal box at the base of the chimney. The extent of background contamination is illustrated by the data in Table 2. These data were obtained with the generator operating under the following conditions: pressure of hydrogen, 15 mmHg; pressure of oxygen, 517 mmHg; concentration of sulfuric acid solution, 0.001 N; aspiration rate, 0.8 ml/min; temperature at filter, 45°C; sampling rate, 15 l/min; and sampling time, 150 min. Three of the sixteen filters were analyzed for acidity by the bromophenol blue method and the rest were analyzed for total sulfate by the barium chloranilate method.

TABLE 2. DATA ILLUSTRATING BACKGROUND CONTAMINATION OF SULFURIC ACID AEROSOL COLLECTED ON MITEX FILTERS

Dilution air	Concn of sulfate in aerosol, as H ₂ SO ₄ , µg/m ³	
	Sample filter	Reference filter
Unfiltered air ^a	29	31
	32	32
	31	32
	1 ^c	32
	-	32
average	-	32
Filtered air ^b	29	28
	26	25
	0 ^c	26
	1 ^c	26
	-	26
average	-	26

^aRoom air was used for dilution of the aerosol.

^bAir filtered through the system described in the text was used for dilution of the aerosol.

^cThese analyses were conducted by the bromophenol blue method for the determination of acidity. All other analyses were conducted by the barium chloranilate method for total sulfates.

The filtering system is illustrated in Figure 1. It consisted of a glass wool prefilter, a Lamb Electric Model 11250 vacuum cleaner blower, a Mine Safety Appliances Ultra Aire No. 82177 absolute filter, and an open-top metal box 25-cm i.d. by 30-cm high. A positive flow of filtered air out of the top of the metal box prevented unfiltered room air from entering the chimney.

The data in Table 2 show that agreement between total sulfate concentrations was good when two filters were collecting samples simultaneously (sample and reference filters). However, the measurements of acidity on three of the filters suggested that all of the sulfuric acid had been essentially neutralized by alkaline gaseous substances in either the filtered or the unfiltered air, presumably by ammonia or amines. Also, the difference between the averages of total sulfate found with filtered and unfiltered air indicated that the background air contained about $6 \mu\text{g}/\text{m}^3$ of particulate sulfate.

The filtering system was then further modified by adding a scrubber to remove alkaline gases. The scrubber consisted of a 4.3-cm Pyrex tube filled to a depth of 24 cm with small Berl saddles that had been impregnated with phosphoric acid. When Mitex filters exposed to the aerosol generated in this system were analyzed for acidity and for ammonium ion, it was found that the phosphoric acid scrubber was partially effective in reducing the background concentration of ammonia.

At this point a decision was made to abandon efforts to work with an aerosol at a concentration of 30 to $40 \mu\text{g}/\text{m}^3$, or less, and to undertake a modified approach based on the use of an aerosol at a concentration high enough so that the background concentrations of contaminants would be negligible compared with the concentration of sulfuric acid. In this modified approach the concentration of sulfuric acid was increased to about $300 \mu\text{g}/\text{m}^3$ and the sampling time was reduced to 10 to 20 min. In this way the total quantity of dilution air was reduced by a factor of about 20, and the total amounts of the background contaminants reaching the Mitex filters were correspondingly reduced.

The performance of the generator system operated at the $300 \mu\text{g}/\text{m}^3$ concentration level is illustrated by the data in Table 3. The results of the measurements of acidity (as H_2SO_4) by the bromophenol blue method were generally in good agreement with the measurements of total sulfate (as H_2SO_4) by the barium chloranilate method. A small difference between the amounts of sulfuric acid collected on the sample and reference filters still existed, however. Other data obtained on other occasions showed that acidity (as H_2SO_4) was usually 80 to 90% of total sulfate (as H_2SO_4). These results indicated that interference by background ammonia was essentially eliminated by operating the generator at a higher concentration and sampling for a shorter period of time.

TABLE 3. MEASUREMENTS OF ACIDITY AND TOTAL SULFATE ON
MITEX FILTERS COLLECTING A 300- $\mu\text{g}/\text{m}^3$ SULFURIC
ACID AEROSOL

Experiment No.	Concn of H_2SO_4 feed solution, equiv./l	Sampling time, min	Amount of H_2SO_4 deposited on filter, μg	
			Sample filter ^a	Reference filter ^b
1	0.02	10	138	188
2	0.01	10	88	89
3	0.005	15	75	81
4	0.005	10	46	48
5	0.005	10	45	44
6	0.005	10	48	48
7	0.005	10	48	51

^a Acidity determined by the bromophenol blue method.

^b Total sulfate determined by the barium chloranilate method.

Sulfur Dioxide in Generator Output

Thomas *et al.*¹ reported that their sulfuric acid aerosol generator did not produce detectable amounts of sulfur dioxide as measured by the West-Gaeke method. A similar result was obtained on this project when the West-Gaeke method was used. However, additional experiments showed that the West-Gaeke method is not applicable to the determination of sulfur dioxide in the combustion products of the hydrogen-oxygen flame.

When a known amount of sulfur dioxide gas was introduced into the aerosol generator through the septum in the sampling probe (see Figure 1) with the burner off, it could be measured satisfactorily. That is, the amount of sulfur dioxide found at the point corresponding to the location of the filter holder was equal to the amount introduced through the septum. However, when the burner was on and the combustion products of the flame were present, no sulfur dioxide could be detected at the location of the filter holder. Also, when the burner was on, and the tetrachloromercurate absorbing solution was spiked with known amounts of sodium bisulfite, either before or after sampling, no sulfur dioxide was detected. In these analyses, procedures recommended for the elimination of interference by nitrogen dioxide, ozone, and heavy metals were followed. These experiments indicated that, whether or not sulfur dioxide was added to the generator gas, it could not be detected because of interfering reactions that occurred in the tetrachloromercurate reagent solution.

In further experiments, sulfur dioxide was injected into the sampling line through the septum and measured at the point corresponding to the downstream location of the filter by means of gas chromatography with a flame photometric detector. With the burner off, the expected amount of sulfur dioxide was found; with the burner on, no sulfur dioxide was detected. This result suggested that sulfur dioxide was rapidly oxidized in the presence of the combustion products of the flame, presumably by the nitrogen dioxide generated in the flame. It is possible, therefore, that the small difference between acidity and total sulfate (as H_2SO_4) shown in Table 3 may have been the result of oxidation of background sulfur dioxide.

Thus, even though Thomas et al. would not have detected sulfur dioxide in the aerosol by the West-Gaeke method if it had been present, they apparently were correct in stating that it was not present. These findings made questionable the use of the hydrogen-oxygen flame generator in studies of the effect of introducing sulfur dioxide directly into the sulfuric acid aerosol.

ANALYTICAL METHODS

The principal analytical methods used in this work were the bromophenol blue method for the determination of acidity,² the barium chloranilate method for the determination of total sulfate,^{3,4} and the benzaldehyde extraction method⁵ coupled with a barium-Thorin titration procedure⁶ for the specific determination of sulfuric acid. The procedures described in the literature were modified somewhat to meet the needs of this project.

The bromophenol blue and barium chloranilate methods were selected for use in the early stages of the project. These methods were effective in most of the instances in which they were applied, but both had certain limitations. The bromophenol blue method is useful only for determination of total acidity and does not distinguish strong acids from most weak acids; also, the sensitivity and precision are less than were desired for this work. The barium chloranilate method was found to be subject to interference by sulfite ion, a point not adequately covered in the literature. The detailed procedures for these methods are described in the following paragraphs.

Bromophenol Blue Method

For determination of acidity by the bromophenol blue method, filters were cut into 0.5-cm strips and placed in a 10-ml volumetric flask containing 2 ml of 80% isopropanol and 1.00 ml of a 0.01% aqueous solution of bromophenol blue. The contents of the flask were mixed on a vortex mixer, diluted to volume with distilled and deionized water, and mixed again. The absorbance of the solution, which decreased nonlinearly with increasing acidity, was measured at 592 nm in a 1-cm cell with a Beckman Model DU

spectrophotometer. Distilled water was used in the reference cell. A calibration curve was prepared by an identical procedure with known volumes of standard solutions of sulfuric acid in the presence of the filter medium. The method was useful for the determination of acidity (as H_2SO_4) over the range of 5 to 40 μg per filter without dilution of the sample. However, poor reproducibility at the limit of detection required that calibration curves be prepared with each set of samples for analysis by this method.

Barium Chloranilate Method

For the determination of sulfate by the barium chloranilate method, a filter sample was placed in a 125-ml screw-capped Erlenmeyer flask containing about 25 mg of barium chloranilate and 10.00 ml of 80% isopropanol. The sample was then mixed for 30 min on a rotary shaker, centrifuged, and the absorbance of the resulting solution measured at 310 nm in a 1-cm fused-silica cell with a Beckman Model DU spectrophotometer. An 80% isopropanol solution was used in the reference cell. A linear calibration curve was prepared with known quantities of standard sulfuric acid solution that were treated in the same manner as experimental samples. The useful range of the method was 10 to 50 μg of sulfuric acid per filter without dilution of the sample. The barium chloranilate method exhibited better reproducibility than the bromophenol blue method for determinations of sulfuric acid, although neither method was specific for sulfuric acid.

Benzaldehyde Extraction Method

It was found that the bromophenol blue and barium chloranilate methods were not compatible with the benzaldehyde extraction of sulfuric acid. No meaningful data could be obtained from analyses of the aqueous extracts of known, dilute solutions of sulfuric acid in benzaldehyde by either method. It appeared that the strong uv absorption of benzaldehyde precluded the spectrophotometric measurement of chloranilic acid at 310 nm in the barium chloranilate method and that the presence of benzoic acid ($\text{pK}_a \approx 4.1$) in benzaldehyde introduced uncertainties in the acidity measurements by the bromophenol blue method. Attempts to remove the residual acidic material from benzaldehyde with an alkaline wash (aqueous sodium carbonate solution) achieved only limited success because of the variable and fairly rapid air oxidation of benzaldehyde to benzoic acid.

Consequently, the microtitration of sulfate with barium perchlorate employing the Thorin indicator was investigated for the determination of sulfuric acid extracted from filters with benzaldehyde. An adaptation of the method reported by Fritz and Yamamura⁶ was used initially to quantitate the sulfate present in aqueous extracts of known solutions of sulfuric acid in benzaldehyde. The results of these preliminary experiments

demonstrated a recovery of sulfuric acid of approximately 90% (including the aqueous extraction step) with a relative standard deviation of less than 5%. The minimum quantity of sulfuric acid that could be determined with the method was found to be approximately 5 µg.

The procedure that evolved for the assay of sulfuric acid on Mitex filters consisted of the following steps:

A 47-mm filter sample was extracted with 5-ml of freshly-distilled (dry and colorless) benzaldehyde; the resulting extract was then centrifuged to separate particulates and a 3-ml portion of the benzaldehyde solution was back-extracted with 1.5 ml of distilled water; a 1.0-ml aliquot of the aqueous extract was then treated with a cation-exchange resin, diluted with 2-propanol, and titrated with a solution of barium perchlorate in 80% 2-propanol, employing the Thorin indicator for end-point detection.

In order to establish the selectivity of the benzaldehyde extraction, several filters were spiked with potentially interfering substances and analyzed by the procedure described above. Solutions or suspensions of ammonium bisulfate, ammonium sulfate, and calcium sulfate in methanol were each spiked onto Mitex filters with a microliter syringe. Because of the residual water content of the benzaldehyde that was used in the extractions, highly variable results were obtained in the initial experiments. Subsequently, however, consistent results were achieved with the use of freshly-distilled benzaldehyde stored under dry nitrogen to exclude water and to minimize air oxidation. Thus, the later results demonstrated that none of these potential interferents was recovered with benzaldehyde extraction in excess of 5% of the amount added to the filter. The spikes of ammonium bisulfate, ammonium sulfate, and calcium sulfate covered the range of 15 to 100 µg per 47-mm filter disk and at this level posed no interference in the specific determination of small amounts of sulfuric acid.

In subsequent studies of the stability of sulfuric acid aerosol deposited on filters with other materials, blank determinations with interferent materials and determinations of sulfuric acid spikes added to benzaldehyde extracts of filters were employed to insure the validity of the results.

Other Analytical Methods

Other analytical methods that were used in the course of this work included the following:

- Ammonia was determined by the indophenol method described by Harwood and Kuhn.⁷ This method could not be used for the determination of ammonia in the generator output because of interference apparently caused by nitrogen dioxide.

- Ammonia was also measured by use of the Orion Model 95-10 ammonia electrode.
- Nitrogen dioxide was determined by the Griess-Saltzman method.⁸
- Sulfur dioxide was measured by the West-Gaeke method⁹ and by gas chromatography with a flame photometric detector.

SELECTION OF FILTER MATERIAL

No systematic evaluation of filter materials was undertaken on this project. The experimental work on comparison of filters that was undertaken early in the project was somewhat beclouded by uncertainties in the analytical procedures and in the composition of the generator effluent. Some later data is of interest, however, and will be described briefly.

Several types of filter materials were considered. They included Millipore HA filters (mixed cellulose esters, pore size 0.45 μm); Mitex LS filters (Teflon fiber mat, pore size 5.0 μm); Versapor filters (glass fibers and epoxy resin, pore size 0.9 μm); Fluoropore FH filters (Teflon bonded to a polyethylene scrim, pore size 0.5 μm); and Nuclepore filters (polycarbonate, pore size 0.4 μm). The Millipore HA filter was recommended for the collection of sulfuric acid aerosol by Thomas et al.¹ The Mitex filter was preferred by Leahy⁵ but was rated by Thomas as among the least effective for the collection of sulfuric acid. Liu and Lee reported on the efficiencies of several types of filters for collecting small particles, and found that Mitex LS collected more than 80% of particles in the size range of 0.03 to 1 μm —in spite of the relative large pore size of 5.0 μm .¹⁰ Glass fiber filters were not considered for sample collection because of the well known problems of alkalinity and reactivity with sulfur dioxide.

Some experiments were conducted to determine the recovery of sulfuric acid spikes added to several types of filters from a microsyringe. (These experiments were of interest in connection with studies involving the use of the bromophenol blue and barium chloranilate methods of analysis but, of course, were not relevant to later experiments involving volatilization and flame photometric measurement of the evolved sulfur compounds.) After measured volumes of diluted sulfuric acid solutions were deposited on the filters (and on glass slides for control), the filters were extracted with 80% isopropanol and the sulfate was determined by the barium chloranilate method. The recovery was 98% from Mitex LS filters, 93% from Millipore HA filters, 87% from Fluoropore FH filters, and 0% from Versapor filters. Retention of the sulfuric acid by the Versapor filters suggested that some kind of fixation

reaction had occurred and that these filters could possibly be used as the basis for a selective method of measuring sulfuric acid aerosol.

The resistance to airflow of 47-mm Mitex filters was found to be 80 mmHg at a flow rate of 15 l/min; that of Fluoropore FH filters was 210 mmHg at the same flow rate.

A principal determining factor in the final selection of Mitex LS filters for use on this project was the fact that this material was also being used by other Environmental Protection Agency contractors who were engaged in closely related research aimed at development of a flame photometric method for determining sulfuric acid aerosol. Also, the limited evaluations conducted on this project indicated that the Mitex filters were the best among those available and tested.

FLAME PHOTOMETRIC DETECTION OF VOLATILIZED SULFURIC ACID

Apparatus

Experiments involving the use of a flame photometric detector for the estimation of sulfuric acid were conducted with a modified Meloy Laboratories Model SA 160-2 Sulfur Gas Analyzer. It was necessary to make several modifications to the Meloy instrument and to the sample flow system before acceptable results could be obtained. Most of the plumbing and the electrometer of the Meloy instrument were eliminated. The Meloy sampling pump was replaced with a source of compressed air. The output current of the photo-multiplier tube was fed into a linear current-voltage amplifier having an amplification factor of 10^5 V/A and an output of 0 to 15 V. The amplifier, therefore, facilitated the measurement of photo-multiplier currents of 0 to 150 μ A. A narrow band-pass filter (394 nm) was used for the specific detection of sulfur. The heater in the detector block was replaced with one capable of maintaining the temperature of the block at 200°C.

A schematic diagram of the system is shown in Figure 2. Fuel and air were supplied to the flame photometric detector at flow rates of 140 and 200 ml/min, respectively. The airflow system was equipped with three manually operated valves. One three-way valve served as a vent to prevent a backflow of air through the sample compartment during the loading operation. A second valve, the sample valve, isolated the sample compartment from the airflow system until it was appropriate to sweep the volatilized material from the sample compartment into the flame photometric detector. A third valve, the bypass valve, was not used routinely. Its purpose was to block the alternate path of air to the burner and to force all of the air through the sample compartment. The timing involved in opening the sample valve and closing the bypass valve was found to be critical. Improper timing resulted in the loss of several samples because of "flame-outs"; therefore, the bypass

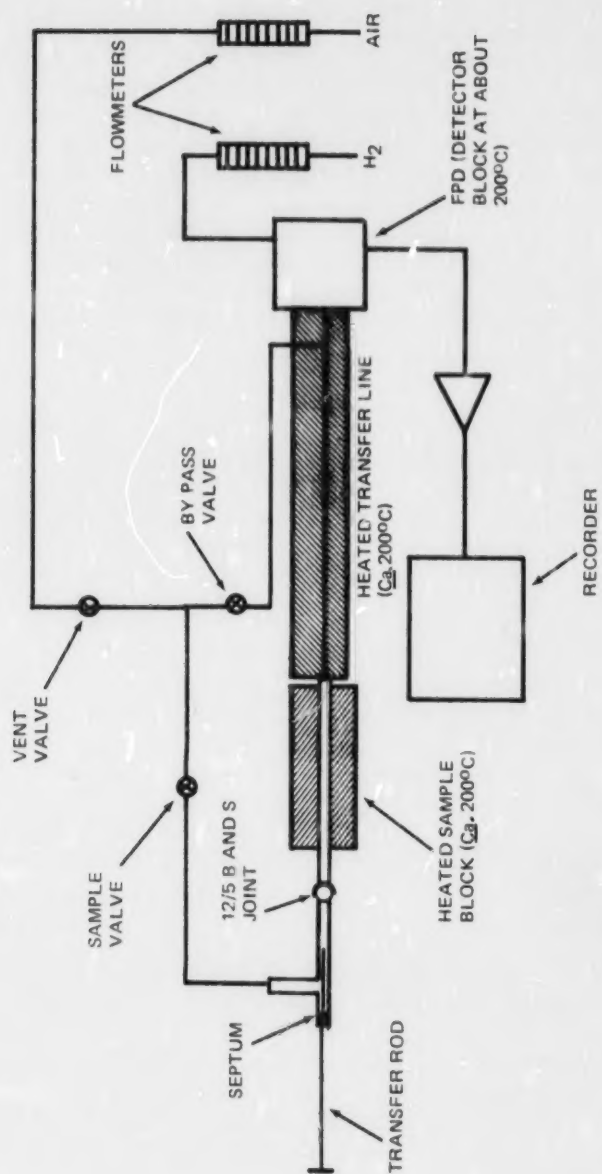


Figure 2. Schematic Diagram of Volatilization-Flame Photometric Apparatus

valve was usually left open. It was estimated that half of the air (ca. 100 ml/min) flowed through the sample compartment when the sample and the bypass valves were open.

Copper tubing was used to connect the air supply to the vent valve. Stainless steel tubing was used between the bypass valve and the flame photometric detector. Glass or Teflon tubing was used in the remainder of the system. The sample compartment was a glass 12/5 ball joint fitted into a heated aluminum block and connected to the flame photometric detector by means of a heated Teflon transfer tube. Stainless steel unions were used to make glass-to-Teflon and Teflon-to-metal joints. The temperatures of the sample block, the transfer tube, and the detector block were monitored by use of Chromel-Alumel thermocouples with 0°C reference junctions. These temperatures were usually between 200 and 210°C, although some experiments were done with the sample block at 150°C.

Sample Loading Procedure

Details of the loading procedure were as follows:

- With the vent valve open and the sample valve closed, the 12/5 ball-and-socket joint connecting the loading compartment to the sample compartment was disconnected and the stainless steel transfer rod was retracted through its septum seal.
- The sample, on a 7.3-mm diameter disk cut from a Mitex LS filter, was placed in the end of a "carry" tube and put into the loading compartment. The "carry" tube was an 85-mm length of Pyrex tubing with an o.d. of 4.5 mm and an i.d. of 3.4 mm.
- The loading compartment was then connected to the sample compartment, the vent valve was closed, and the hydrogen flame was ignited.
- The sample was then moved into the heated sample compartment with the transfer rod, and a timer was started.
- After a predetermined hold time at the test temperature, the sample valve was opened and the volatilized material was swept into the flame photometric detector. A hold time of 1 min was customary at 200°C while a 2-min hold time was used at 150°C.

Calibration with Known Amounts of Sulfuric Acid

Initial flame photometric measurements were made with 7.3-mm diameter sample disks cut from Mitex LS filters and spiked with known amounts of sulfuric acid. A standard solution containing

1.9 $\mu\text{g}/\mu\text{l}$ of sulfuric acid in 2-propanol was applied to the Teflon filter with a microsyringe. Standard filter disks were prepared by putting 1.0, 1.5, or 2.0 μl of this solution on the disks and evaporating the solvent under nitrogen. The sample disks were stored under nitrogen until they were loaded into the sample block. To facilitate the comparison of the results, all responses were recorded on the 0 to 500 mV range of a Hewlett Packard Model 7128A strip-chart recorder. The chart speed was 1 in./min. The test temperature was 200°C and the hold time was 1 min.

Although the square root of the area under the response curves obtained with standard samples would be the most appropriate parameter, the square root of peak height was taken to be a convenient measure of the concentration of sulfuric acid. The results of these measurements are given in Table 4.

TABLE 4. CALIBRATION DATA FOR THE FLAME
PHOTOMETRIC DETECTOR^a

Amount of H_2SO_4 , μg	Number of measurements	(Peak height) ^{1/2} , arbitrary units, average ^b	Relative standard deviation, %
1.9	9	5.9	4.1
3.8	3	7.0	4.7

^a Detector responses were obtained under the conditions described in the text. The test temperature was 200°C.

^b These data do not show the expected dependence on concentration; i.e., peak area should be proportional to the square of sulfur mass concentration.

Tracings of typical response curves for standard samples are shown in Figure 3. No response was obtained with blank 7.3-mm disks that were cut from Mitex LS filters and handled in the same manner as the standard samples except for the addition of the sulfuric acid spike. The principal sulfuric acid peak occurred almost immediately after the sample valve was opened. A feature of all of the data collected with the flame photometric apparatus was the appearance of a small secondary peak that occurred after the sample valve had been closed for several minutes and then reopened. This secondary peak was attributed to the retention of traces of sulfuric acid on the filter and the slow evolution of this residual with time.

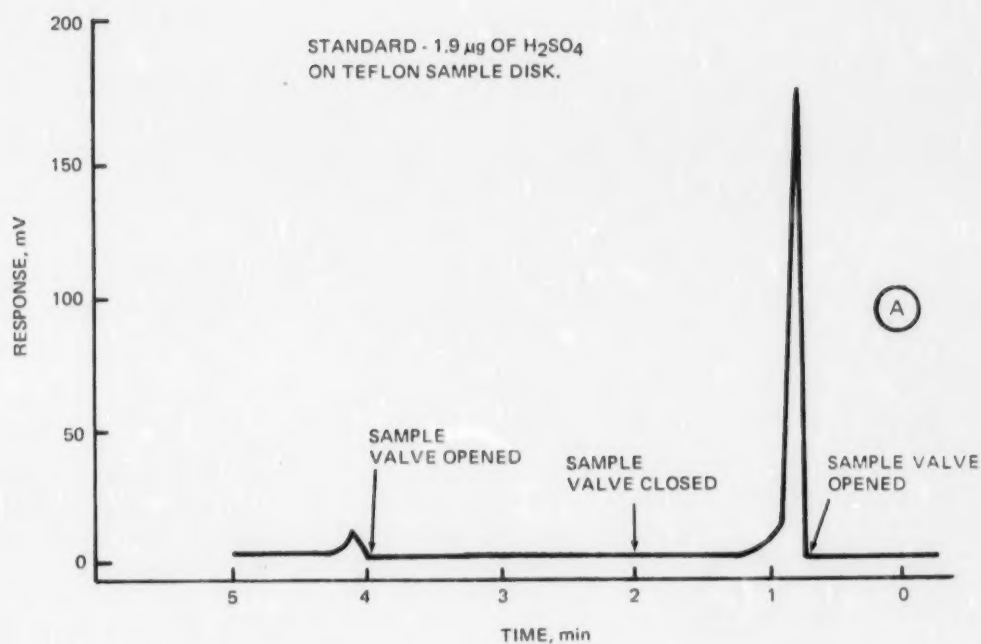
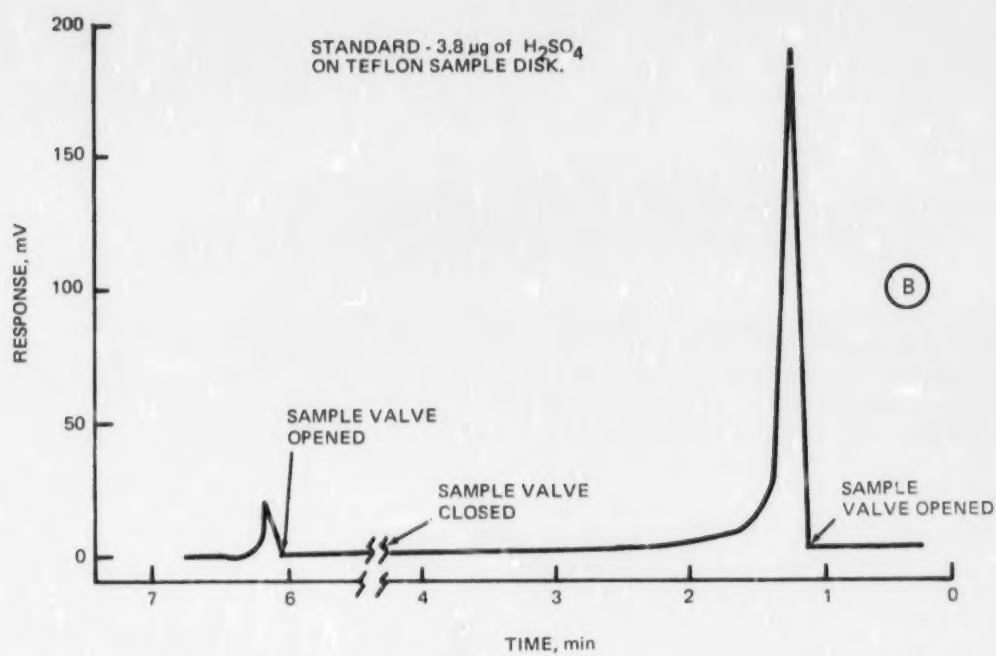


Figure 3. Flame Photometric Response to Standard Samples of Sulfuric Acid.
Temperature, 200°C.

Comparison of Flame Photometric and Benzaldehyde Extraction Procedures

Several Mitex LS filters were loaded with equal amounts of sulfuric acid aerosol. Sulfuric acid was determined on three filters by the benzaldehyde extraction technique previously described. The average amount of sulfuric acid on these filters was 66 μg . Three 7.3-mm diameter sample disks were cut from another filter for the flame photometric determination of sulfuric acid. One disk was cut from the center of the collection filter and two were cut from areas adjacent to the center. The effective area of the 47-mm diameter collection filter was assumed to be the area directly over the grid of the support plate in the filter holder. The diameter of this grid was 35 mm; therefore, the effective area of the filter was 962 mm^2 and each small sample disk represented about 4.3% of the total effective area. The average of square roots of the flame photometric responses for these samples was 6.6 units. The relative standard deviation was 2.9%. The samples were run under conditions identical to those used for the calibration. Reference to the calibration data given in Table 4 showed that the average amount of sulfuric acid on the small sample disks was 2.9 μg . The total amount of sulfuric acid on the collection filter was then calculated to be 67 μg . The agreement between the two methods was excellent: sulfuric acid by flame photometric detection = 67 μg ; sulfuric acid by benzaldehyde extraction = 66 μg . In view of the approximation used to correlate flame photometric response with the concentration of sulfuric acid and the possible retention of sulfuric acid on filters, the agreement between the two different determinations of sulfuric acid was better than expected.

SECTION 5

RESULTS OF INTERFERENCE STUDIES

GAS AND VAPOR INTERFERENTS

Introduction of Gases Directly into Sulfuric Acid Aerosol

In the earlier stages of this project experiments were conducted in which sulfur dioxide, nitrogen dioxide, or ammonia was introduced directly into the sulfuric acid aerosol. In these first experiments the generator was operated to give concentrations of sulfuric acid of about 20 to 50 $\mu\text{g}/\text{m}^3$ and the interferent gases were introduced at known concentrations into the side arm of the sampling probe (Figure 1). Analyses for acidity and total sulfate were made by the bromophenol blue and barium chloranilate methods, respectively. These experiments were generally inconclusive because of problems in measuring sulfur dioxide concentrations in the generator gas (see page 16), the production of nitrogen dioxide by the flame (see page 12), and uncertainties caused by the presence of varying concentrations of background ammonia. The results that were obtained, however, gave some indications that neither sulfur dioxide nor nitrogen dioxide interfered in the measurement of sulfuric acid when significant amounts of other substances were absent.

Sulfur Dioxide. Analyses by Bromophenol Blue and Barium Chloranilate Methods--

The most meaningful experiments with sulfur dioxide were conducted by adding sulfur dioxide at a concentration of 200 $\mu\text{g}/\text{m}^3$ to sulfuric acid aerosol at a concentration of about 300 $\mu\text{g}/\text{m}^3$. The results shown in Table 5 indicate that the addition of sulfur dioxide to the aerosol apparently had little effect on the amount of sulfuric acid collected on the filters, whether measured as acid or as sulfate. This conclusion cannot be adequately reconciled, however, with the results of other experiments which indicated that sulfur dioxide is at least partly oxidized to sulfate by the combustion products derived from the flame. One possible explanation for no apparent oxidation of sulfur dioxide may relate to the lower concentration of nitrogen dioxide in the generator effluent that occurred at the lower flame temperatures used in these experiments.

TABLE 5. RESULTS OF EXPERIMENTS IN WHICH SULFURIC ACID AEROSOL WAS COLLECTED ON MITEX FILTERS IN THE PRESENCE OF SULFUR DIOXIDE^a

Run No.	Total H ₂ SO ₄ deposited, μg ^b			
	Determined as acid		Determined as sulfate	
	Reference		Reference	
	Sample filter (SO ₂ added)	filter (SO ₂ not added)	Sample filter (SO ₂ added)	filter (SO ₂ not added)
1	49	52	-	-
2	-	-	55	58
3	54	49	-	-
4	-	-	55	60
5	48	46	-	-
6	50	45	-	-
7	-	-	52	56
8	47	50	-	-
9	-	-	55	54
Av	50	58	54	57

^a Generator and sampling conditions: H₂, 15 mmHg; O₂, 103 mmHg; Ar, 627 mmHg; aspiration rate, 3 ml/min; probe temperature, 60°C; feed solution, 2×10^{-3} N H₂SO₄; sampling rate, 6 l/min; total volume sampled, 0.120 m³. The SO₂ concentration was approximately 200 $\mu\text{g}/\text{m}^3$.

^b Acidity was determined by the bromophenol blue method. Sulfate was determined by the barium chloranilate method.

Nitrogen Dioxide. Analyses by Bromophenol Blue and Barium Chloranilate Methods--

These experiments were done by exposing Mitex LS filters simultaneously to nitrogen dioxide and sulfuric acid aerosol. The average concentration of nitrogen dioxide was 320 $\mu\text{g}/\text{m}^3$ and the average concentration of sulfuric acid was 366 $\mu\text{g}/\text{m}^3$ (determined as SO₄⁻²) and 300 $\mu\text{g}/\text{m}^3$ (determined as acid). About 40 μg of sulfuric acid was collected on each filter and about 40 μg of nitrogen dioxide was introduced into each sampling line over the sampling period. The results are given in Table 6. They indicate that nitrogen dioxide had no effect on the collection of sulfuric acid. No complicating phenomena were observed in these experiments; however, some nitrogen dioxide, in addition to that added, was assumed to be present as a result of its formation in the flame.

TABLE 6. RESULTS OF EXPERIMENTS IN WHICH SULFURIC ACID AEROSOL WAS COLLECTED ON MITEX FILTERS IN THE PRESENCE OF NITROGEN DIOXIDE^a

Run No.	Total H ₂ SO ₄ deposited, μg ^b			
	Determined as acid		Determined as sulfate	
	Sample filter (SO ₂ added)	Reference filter (SO ₂ not added)	Sample filter (SO ₂ added)	Reference filter (SO ₂ not added)
1	-	-	43	46
2	33	33	-	-
3	-	-	38	41
4	38	39	-	-
Av	36	36	40	44

^a Generator and sampling conditions: H₂, 15 mmHg; O₂, 103 mmHg; Ar, 672 mmHg; aspiration rate, 2.6 ml/min; probe temperature, 60°C; feed solution, 2×10^{-3} N H₂SO₄; sampling rate, 6 l/min; total volume sampled, 0.120 m³. The NO₂ concentration was 320 $\mu\text{g}/\text{m}^3$.

^b Acidity was determined by the bromophenol blue method. Sulfate was determined by the barium chloranilate method.

Introduction of Gases and Vapors onto Filters Preloaded with Sulfuric Acid Aerosol

Ammonia. Analyses by Bromophenol Blue and Barium Chloranilate Methods--

The apparatus shown in Figure 4 was constructed in order to expose filters preloaded with sulfuric acid aerosol to gaseous interferences. Mitex filters preloaded with sulfuric acid were put into the sample and reference filter holders. Room air was drawn through a 40% solution of sulfuric acid, a Gelman Type AE filter, and the sample and reference filters. The sampling rate was 6 l/min through each filter. The solution of sulfuric acid removed alkaline gases from the ambient air and also served to maintain the relative humidity of the sample air at about 50%. The function of the Gelman Type AE filter was to remove any sulfuric acid mist that might be entrapped in the sample air. Blank runs showed that no detectable sulfuric acid mist escaped the Gelman filter. The interferent was introduced through a tee located about 18 cm in front of the sample filter.

In one experiment equivalent amounts (34 μg , or 0.70 μ equiv) of sulfuric acid were deposited on each of two filters. One filter was then exposed to sample air (at 6 l/min for 5 min) containing a total of 3.5 μg (0.20 μ equiv) of ammonia. The other

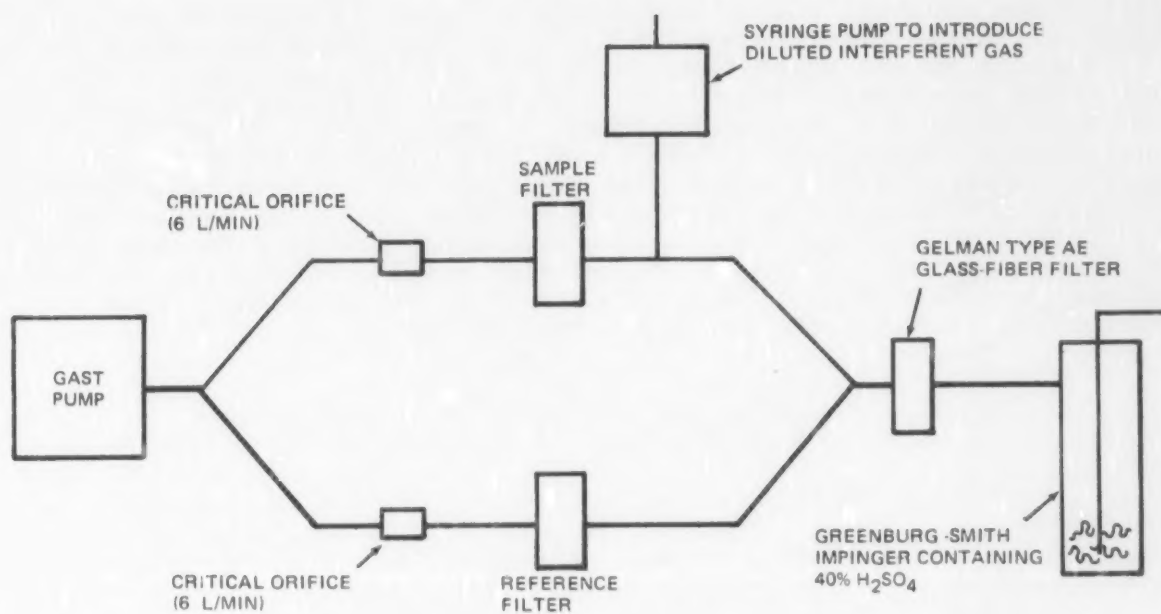


Figure 4. Apparatus for Exposure of Preloaded Filters to Ammonia

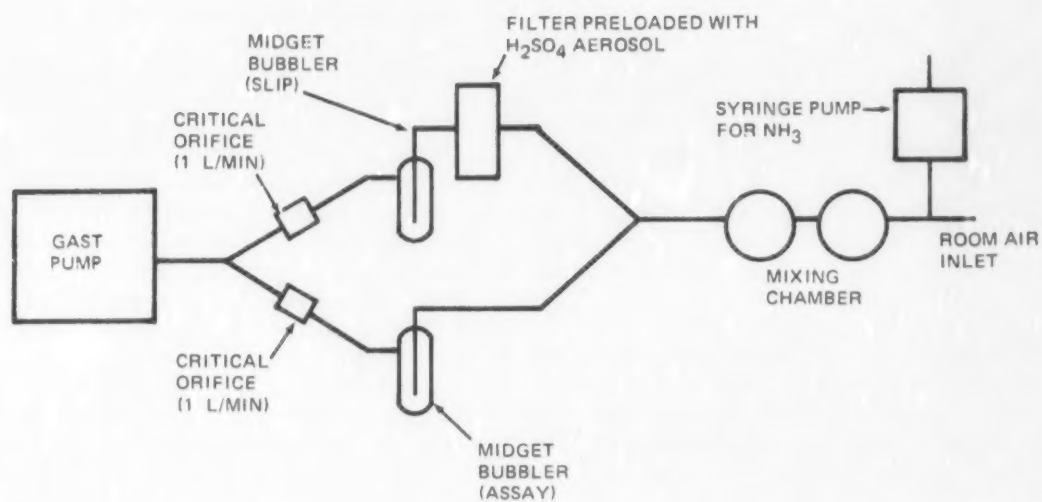


Figure 5. Modified Apparatus for the Exposure of Preloaded Filters to Ammonia

filter was exposed to the same sample air but without the added ammonia. After the exposure, acidity was determined on each of the filters by the bromophenol blue method. The reference filter was found to contain 34 μg (0.70 μ equiv) of sulfuric acid while the sample filter (exposed to ammonia) contained 17 μg (0.35 μ equiv) of sulfuric acid. From these data it was calculated that approximately 50% of the sulfuric acid was neutralized; the amount neutralized, however, was greater, in terms of equivalents, than the amount of ammonia added. This result is explainable only on the basis of the presence of background ammonia in the 120 liters of air sampled—which is unlikely since it had been shown that ammonia was not present in this scrubbed air—or on the basis of errors in measurement.

The experiment was repeated with 45 μg (0.90 μ equiv) of pre-deposited sulfuric acid and 2.5 μg (0.14 μ equiv) of added ammonia. The sample filter (exposed to ammonia) was found to contain 35 μg (0.70 μ equiv) of sulfuric acid by the bromophenol blue method. The amount of sulfuric acid neutralized was again greater than the amount of ammonia added, in terms of equivalents.

Additional experiments were done in which ammonia (0.14 and 0.12 μ equiv) was introduced onto filters preloaded with 53 μg (1.08 μ equiv) of sulfuric acid and the filters analyzed for sulfate by the barium chloranilate method. As expected, the exposure to ammonia did not affect the results obtained by determining total sulfate.

Ammonia. Analysis by the Benzaldehyde Extraction Method--

In these experiments benzaldehyde extraction and Ba-Thorin microtitration were used for sulfuric acid determination and the amounts of ammonium ion retained on filters and amounts of ammonia passing through the filters were determined. Also, the modified apparatus depicted schematically in Figure 5 was used to expose filters preloaded with sulfuric acid aerosol to ammonia. In this apparatus ammonia diluted with nitrogen was added from a syringe pump into an ambient airstream; the airstream was then passed through a mixing chamber. The flow was split equally for determination of ammonia concentration in one arm and for exposure to preloaded filters and measurement of slippage through the filters in the other arm. It was determined that a single bubbler containing dilute sulfuric acid was sufficient for quantitative collection of the ammonia from the airstream in either arm. The range of ammonia concentrations used for exposure to filters preloaded with sulfuric acid aerosol was 0.13 to 1.9 mg/m^3 and the sampling times were approximately 20 min at a flow rate of 1 l/min.

The results are presented in Table 7. In terms of micro-equivalents (μ equiv) these data show a reasonably good correlation between amount of sulfuric acid lost upon exposure to ammonia and the amount of ammonium ion found on the filters. Also, slip of ammonia through filters loaded with sulfuric acid aerosol was significant only in the instances where the ratio of microequivalent of ammonia to microequivalent of sulfuric acid exceeded 1.0. In these instances the sulfuric acid was completely lost. In the experiments where the amounts of ammonia were less than stoichiometric, the amount of sulfuric acid lost correlated fairly well with the amount of ammonia to which the filter was exposed.

On the basis of these results it can be concluded that sulfuric acid aerosol collected on a Mitex filter will be consumed stoichiometrically by ammonia with the formation of ammonium sulfate on the filter. This conclusion was evidenced by the excessive slip of ammonia after the formation of ammonium sulfate on the filters for which the ratio of ammonia to sulfuric acid exceeded 1.0.

Obviously, these data suggest that an alkaline gas such as ammonia can cause a loss of sulfuric acid during the collection of sulfuric acid aerosol on a filter.

TABLE 7. EFFECT OF AMMONIA ON PREDEPOSITED SULFURIC ACID
AEROSOL ON MITEX LS FILTERS

NH ₃ added, ^a μ equiv	H ₂ SO ₄ aerosol added, μ equiv ^b	Ratio NH ₃ /H ₂ SO ₄	NH ₃ or NH ₄ ⁺ Filter	Slip	Total μ equiv ^c	H ₂ SO ₄ found, ^d μ equiv	H ₂ SO ₄ lost, ^e μ equiv
0.15	1.04	0.14	0.12	0.05	0.17	1.06	0
0.25	0.77	0.32	0.23	0.03	0.26	0.53	0.24
0.41	0.80	0.51	0.33	0.03	0.36	0.49	0.31
0.52	0.76	0.68	0.29	0	0.29	0.57	0.19
1.50	0.84	1.79	0.79	0.13	0.92	0	0.84
2.26	0.86	2.63	1.04	0.91	1.95	0	0.86

^a The quantity of ammonia exposed to each filter was determined by analysis of a parallel bubbler by the indophenol method. One microequivalent of NH₃ = 17 μg.

^b The quantity of sulfuric acid aerosol predeposited on the filters was determined by analysis of parallel filters exposed only to sulfuric acid aerosol. These analyses were conducted with the benzaldehyde extraction and Ba-Thorin microtitration. One microequivalent of H₂SO₄ = 49 μg.

^c The ammonium ion present on the test filter was determined by extraction of one-half of the test filter with dilute sulfuric acid and measurement by the indophenol method; the other half was reserved for determination of residual sulfuric acid. The ammonia that slipped the test filter was collected in a bubbler containing dilute sulfuric acid and measured also by the indophenol method.

^d These results represent twice the amount of sulfuric acid found upon analysis of one-half the test filter disk.

^e These data represent the difference between the sulfuric acid added and the sulfuric acid found.

Pyridine Vapor. Analysis by the Benzaldehyde Extraction Method--

Pyridine was chosen for the study of potential interference from organic amines. In addition to being an aromatic heterocyclic compound, pyridine is a weaker base ($pK_b \approx 8.8$) than ammonia ($pK_b \approx 4.7$) or typical aliphatic amines ($pK_b \approx 2$ to 5).

The experiments with pyridine vapor were conducted with the same apparatus shown in Figure 5 that was used in identical experiments with ammonia. In the present experiments benzaldehyde extraction and Ba-Thorin microtitration were again used for sulfuric acid determination and the amounts of pyridinium ion retained on filters and amounts of pyridine vapor passing through the filters were determined by a gas chromatographic procedure. The gas chromatographic procedure was based on the injection of aqueous (dilute sulfuric acid) samples containing dissolved pyridine (pyridinium) onto a 1.8-m by 2-mm column packed with 5% potassium hydroxide and 10% Carbowax 20M on a support of Gas Chrom P, employing flame ionization detection. The range of pyridine concentrations used for exposure to filters preloaded with sulfuric acid was 0.28 to 3.8 mg/m³ and the sampling times were approximately 20 min at a flow rate of 1 l/min.

The results are presented in Table 8. In terms of micro-equivalents these data show a poor correlation between the amount of sulfuric acid lost upon exposure to pyridine vapor and the amount of pyridinium ion ($C_5H_5NH^+$) found on the filters. In most cases, the losses of sulfuric acid were very small and the pyridinium ion on the filter exceeded the loss of sulfuric acid. These data demonstrated a much different behavior for pyridine vapor than was found earlier for ammonia. Essentially stoichiometric reaction was observed for ammonia and predeposited sulfuric acid. Because significant amounts of pyridinium ion were found on the filters, it is speculated that the benzaldehyde extraction removed pyridinium bisulfate (or sulfate) from the filters in addition to residual sulfuric acid. In this event the analyses for sulfate in the aqueous back-extract could then lead to high results for sulfuric acid due to the soluble bisulfate. Another explanation—although less likely—concerns the possible adsorption of unreacted pyridine vapor on the filters in the presence of sulfuric acid. This phenomenon could conceivably result in reporting the presence of pyridinium ion from the filter analyses by gas chromatography and sulfuric acid with benzaldehyde extraction. Both hypotheses could be tested by measuring the extractability of authentic pyridinium bisulfate (or sulfate) with benzaldehyde in the first case, and measuring the retention of pyridine vapor by blank Mitex filters in the second case.

TABLE 8. EFFECT OF PYRIDINE VAPOR ON PREDEPOSITED SULFURIC ACID ON MITEX LS FILTERS

C ₅ H ₅ N added, μ equiv ^a	H ₂ SO ₄ added, μ equiv ^b	C ₅ H ₅ N or C ₅ H ₅ NH ⁺ found, μ equiv ^c			H ₂ SO ₄ found, μ equiv	H ₂ SO ₄ lost, μ equiv
		Filter	Slip	Total		
0.07	1.3	0.05	0.02	0.07	1.2	0.1
0.13	1.4	0.11	0.06	0.17	1.5	None
0.17	1.5	0.25	0.03	0.28	1.4	0.1
0.29	1.3	0.27	0.06	0.33	0.9	0.4
0.95	1.1	0.59	0.40	0.99	1.2	None

- The quantity of pyridine to which each filter was exposed was determined by analysis of a parallel bubbler by a gas chromatographic method.
- The quantity of sulfuric acid predeposited on each filter was determined by analysis of a parallel filter exposed only to sulfuric acid aerosol.
- The pyridinium ion present on the test filter was determined by extraction of one-half of the test filter with dilute sulfuric acid and measurement by a gas chromatographic method; the other half was reserved for determination of residual sulfuric acid. The pyridine that slipped the test filter was collected in a bubbler containing dilute sulfuric acid and measured also by a gas chromatographic method.

Ammonia. Analysis by the Flame Photometric Method --

Ammonia interference was also studied with the technique involving thermal volatilization of the sample and flame photometric detection of the evolved sulfur species. In these qualitative experiments, sulfuric acid was collected on a Mitex filter from the aerosol generator, and the filter was subsequently exposed to excess gaseous ammonia over a beaker containing a concentrated aqueous solution of ammonia. Essentially no response was observed with the flame photometric detector upon heating the filter that was exposed to excess ammonia; on the other hand, the expected response was obtained for the reference filter that was not exposed to ammonia.

In addition, no response was obtained with the flame photometric detector upon heating filters that were spiked with ammonium bisulfate either from solution in methanol or as the solid crystalline material.

These data also demonstrate that gaseous ammonia can cause losses of sulfuric acid during sampling, and that the reaction products, ammonium sulfate or bisulfate, do not appear to interfere with determinations of residual sulfuric acid on filters by the flame photometric technique.

Phenol Vapor. Analysis by the Benzaldehyde extraction method --

Experiments with phenol vapor were also conducted with the apparatus shown in Figure 5 that was used for the ammonia and pyridine studies. Bubblers containing 0.01 N NaOH were used for determining the amount of phenol added (parallel bubbler) and the amount of phenol that slipped the filters exposed previously to sulfuric acid aerosol (slip bubbler). The concentrations of phenol in the bubblers were determined by measuring the spectrophotometric absorbance at 287 nm due to the phenolate ion in the alkaline bubbler solution. The analyses for sulfuric acid were performed by the benyaldehyde extraction method.

The results of this study are given in Table 9. These data show that little or no sulfuric acid was lost and that essentially all of the phenol vapor slipped the filters. On the basis of these data phenol does not appear to be a significant interference to the sampling of sulfuric acid aerosol with Mitex filters.

PARTICULATE INTERFERENTS

Analyses by Bromophenol Blue and Barium Chloranilate Methods

Ambient Particulate Material --

Exposure of filters with predeposited sulfuric acid to ambient air -- Each of nine Mitex LS filters was spiked with 50 μ l of a solution containing about 1.04 μ g/ μ l of sulfuric acid. These filters were allowed to stand in a desiccator over silica gel for 24 hr prior to use. After "drying", all of the spiked filters—still in the desiccator—and the necessary sampling equipment were taken to the North Birmingham monitoring station of the Jefferson County Health Department. Two of the spiked filters were used to sample the air for 30 min, and two were used to sample for 50 min. The sampling flow rate was 15.3 l/min. The filters were placed in a desiccator over silica gel immediately after sampling. On the following day, acidity was determined by the bromophenol blue method on all of the test filters and on three control filters. The control filters were spiked and analyzed at the same time as the test filters. The results

TABLE 9. EFFECT OF PHENOL VAPOR ON PREDEPOSITED SULFURIC ACID ON MITEX LS FILTERS

Phenol added, ^a μg	H ₂ SO ₄ added, ^b μg	Phenol found, ^c μg		H ₂ SO ₄ found, μg	H ₂ SO ₄ lost, μg
		Filter	Slip		
20	65	Lost	32	64	1
82	51	<5	90	52	-
112	67	<5	124	68	-
228	77	nd	240	64	13

- The quantity of phenol to which each filter was exposed was determined by analysis of a parallel bubbler (0.01 N NaOH) with a spectrophotometric method.
- The quantity of sulfuric acid predeposited on each filter was determined by analysis of a parallel filter exposed only to sulfuric acid aerosol.
- The amount of phenol on the filters was determined by extraction with 0.01 N NaOH followed by spectrophotometric measurement; the phenol vapor that slipped the filters was determined by spectrophotometric analysis of slip bubblers containing 0.01 N NaOH.

of this experiment are given in Table 10. Although the differences in the amounts of sulfuric acid found on the test filters and the control filters may be within experimental error for Filters 1, 2, 3, and 4 (10- and 30-min sampling times), the difference is certainly real for Filters 5 and 6 (60-min sampling time). It was concluded, therefore, that in this experiment evidence of significant neutralization of the 54 μg of predeposited sulfuric acid occurred during the sampling of approximately 1 m³ of ambient air. One factor affecting the interpretation of these data is that the sulfuric acid could not be uniformly dispersed on the spiked Teflon filters. The spike consisted of 4 to 6 droplets of solution that were 1 to 2 mm in diameter. The aqueous solution did not, of course, wet the Teflon membrane filters. Therefore, the acid was concentrated on a small portion of the filter and most of the air that passed through the filter did not come in direct contact with the deposited acid. One would expect the neutralization of the acid by alkaline materials in the atmosphere to be more pronounced had the filters been spiked uniformly with sulfuric acid aerosol particles.

TABLE 10. EFFECT OF AMBIENT AIR ON
SULFURIC ACID-SPIKED FILTERS

Sample	Volume sampled, m ³	Amount of H ₂ SO ₄ found, μg ^a	Amount of H ₂ SO ₄ on test filter minus amount on control filter ^b
Control	0	55	-
Control	0	53	-
Control	0	55	-
1	0.153	55	+1
2	0.153	58	+4
3	0.459	53	-1
4	0.459	53	-1
5	0.918	42	-12
6	0.918	38	-16

a. Determined by the measurement of acidity by the bromophenol blue method.

b. The average amount of sulfuric acid found on the control filters was 54 μg. The calculated amount deposited was 52 μg.

Exposure of filters with predeposited ambient particulate material to sulfuric acid aerosol--Particulate material was collected on Mitex LS filters by sampling air for several hours at a location near a busy street. The filters were weighed to determine the amount of particulate material collected. Some of the filters were then exposed to sulfuric acid aerosol from the generator for the period of time required to deposit about 50 μg of sulfuric acid; others were not exposed to the acid. Reference filters, containing no ambient particulate material, were simultaneously exposed to the same sulfuric acid aerosol as the sample filters. The filters were then analyzed by the bromophenol blue or barium chloranilate methods. The results are given in Table 11. Analyses for total sulfate showed that all of the added sulfuric acid was recovered along with the soluble sulfate in the ambient particulate material. However, measurements of acidity indicated that only about 50% of the expected amount of acid was present. Therefore, on the basis of these data, it appeared that a quantitative conversion of sulfuric acid to an equivalent amount of soluble bisulfate occurred.

TABLE 11. EFFECT OF PREDEPOSITED AMBIENT PARTICULATE UPON
THE COLLECTION OF SULFURIC ACID AEROSOL ON
MITEX LS FILTERS

Ambient particulate on filter, mg ^a	H ₂ SO ₄ aerosol added, µg ^b	Total H ₂ SO ₄ found, µg ^c		H ₂ SO ₄ found less SO ₄ ⁻² from particulate, µg	Recovery %
		as SO ₄ ⁻²	as H ⁺		
1.7	none	128	-	-	-
0.9	62	127	-	59 ^d	95
0.7	none	-	nd ^e	-	-
1.4	none	-	nd	-	-
1.0	50	-	20	-	40
2.1	56	-	35	-	63

- a. This particulate material was sampled from the ambient air before the addition of the sulfuric acid aerosol.
- b. The amount of sulfuric acid aerosol added to each filter was determined by analysis of a parallel filter exposed only to sulfuric acid aerosol.
- c. Sulfate was determined by the barium chloranilate method and acid was determined by the bromophenol blue method.
- d. This number resulted from the following calculation:
127 - 128 (0.9/1.7).
- e. nd = not detected.

Calcium Carbonate --

An aerosol of finely powdered calcium carbonate was generated with a DeVilbiss powder blower and about 1 to 3 mg of the dispersed powder was collected on a Mitex filter upon which about 50 µg of sulfuric acid had been predeposited. The results of the analyses of these filters are shown in Table 12. A complete loss of both acidity and soluble sulfate was observed. This result suggested that the predeposited sulfuric acid reacted completely with the excess calcium carbonate forming insoluble calcium sulfate.

TABLE 12. EFFECT OF COLLECTED CALCIUM CARBONATE AEROSOL
UPON PREDEPOSITED SULFURIC ACID
ON MITEX LS FILTERS

CaCO ₃ aerosol added, mg ^a	H ₂ SO ₄ aerosol added, µg ^b	H ₂ SO ₄ found, µg ^c		Recovery, %
		as SO ₄ -2	as H+	
1.4	none	nd ^d	-	-
3.1	none	nd	-	-
1.3	68	0.3	-	<1
3.5	62	0.4	-	<1
0.8	none	-	nd	-
3.3	none	-	nd	-
2.6	44	-	nd	0
3.1	65	-	nd	0

- a. The amount of calcium carbonate was determined by weighing. The calcium carbonate aerosol was added immediately following the collection of the sulfuric acid aerosol and the total sampling time was approximately 20 to 30 min.
- b. The amount of sulfuric acid aerosol added to each filter was determined by analysis of a parallel filter exposed only to sulfuric acid aerosol.
- c. Sulfate was determined by the barium chloranilate method and acid was determined by the bromophenol blue method.
- d. nd = not detected.

Ferric Oxide --

An experiment similar to that described above for calcium carbonate was conducted with a dispersed fine powder of ferric oxide. A small but significant loss of acidity was observed, as shown in Table 13. The average recovery of sulfuric acid, as measured by the bromophenol blue method, was approximately 72%. The average recovery of total added sulfate, as measured by the barium chloranilate method, was substantially higher, approximately 94%. Thus, it appeared that some loss of the predeposited acid occurred, with the formation of an equivalent amount of soluble bisulfate.

TABLE 13. EFFECT OF COLLECTED FERRIC OXIDE AEROSOL UPON
PREDEPOSITED SULFURIC ACID ON MITEX LS FILTERS

Fe ₂ O ₃ aerosol added, mg ^a	H ₂ SO ₄ aerosol added, µg ^b	H ₂ SO ₄ found, µg ^c		Recovery, %
		as SO ₄ ⁻²	as H ⁺	
0.4	none	nd ^d	-	-
0.6	none	nd	-	-
0.3	28	24	-	86
0.8	37	36	-	97
2.0	80	80	-	100
0.1	none	-	nd	-
0.4	none	-	nd	-
0.4	none	-	nd	-
0.5	none	-	nd	-
0.5	20	-	8	40
0.4	22	-	16	73
0.4	66	-	62	94
1.5	78	-	62	79

- a. The amount of ferric oxide was determined by weighing. The ferric oxide aerosol was added immediately following the collection of the sulfuric acid aerosol and the total sampling time was approximately 20 to 30 min.
- b. The amount of sulfuric acid aerosol added to each filter was determined by analysis of a parallel filter exposed only to sulfuric acid aerosol.
- c. Sulfate was determined by the barium chloranilate method and acid was determined by the bromophenol blue method.

Analyses by the Benzaldehyde Extraction Method

Ambient Particulate Material--

Filters with predeposited ambient particulate material were exposed to sulfuric acid aerosol as described earlier, with analysis, however, by the benzaldehyde extraction-barium Thorin titration procedure. The results in Table 14 show a slight contribution of sulfate (as H₂SO₄) from the particulate material itself; however, the results were below the reproducible limit of detection (reported as <5 µg). The recoveries of spikes added to extracts were adequate (79 and 88%), but the losses of sulfuric acid added to the preloaded filters as aerosol were very significant. The recoveries of sulfuric acid from the filters were

variable and ranged from 29 to 38%. These results were not corrected for the residual sulfate from the particulate, which could have been significant because of the somewhat larger amounts of particulate present on the test filters as opposed to the blank filters. Therefore, the recoveries could possibly have been even lower than those reported here.

These results are in sensible agreement with those reported earlier in that the formation of bisulfates or possibly sulfates from sulfuric acid appears to take place readily on a filter preloaded with ambient particulate material.

TABLE 14. EFFECT OF PREDEPOSITED AMBIENT PARTICULATE MATERIAL UPON SULFURIC ACID COLLECTED ON MITEX LS FILTERS

Ambient particulate added, mg ^a	H ₂ SO ₄ added, µg ^b	H ₂ SO ₄ spike, µg ^c	H ₂ SO ₄ found, µg	Recovery, %
0.3	none	none	<5	-
0.4	none	none	<5	-
1.7	none	58	46	79
1.2	none	58	51	88
1.8	(lost)	none	5	-
1.9	24	none	9	38
2.1	34	none	10	29

- The amount of ambient particulate material was determined by weighing. The particulate was collected in the vicinity of a busy roadway in Birmingham over a 15-hr period.
- The amount of sulfuric acid added to each filter was determined by analysis of a parallel filter exposed only to sulfuric acid aerosol. The sampling time was 20 to 30 min.
- Analytical spikes of sulfuric acid in benzaldehyde were added to some of the filter extracts that contained suspended ambient particulate.

Calcium Carbonate--

The results of the analyses for sulfuric acid with benzaldehyde extraction that were performed on filters loaded with calcium carbonate are presented in Tables 15 and 16. The data in Table 15 are for exposures of predeposited sulfuric acid aerosol to calcium carbonate aerosol and the data in Table 16 are for

TABLE 15. EFFECT OF CALCIUM CARBONATE AEROSOL UPON
PREDEPOSITED SULFURIC ACID ON MITEX LS FILTERS

CaCO ₃ aerosol added, mg ^a	H ₂ SO ₄ aerosol added, µg ^b	H ₂ SO ₄ spike added, µg ^c	H ₂ SO ₄ found, µg ^d	Recovery, %
1.3	none	none	nd ^e	-
1.6	none	none	nd	-
2.9	none	none	nd	-
2.6	none	none	nd	-
2.8	45	none	11	24
2.8	49	none	12	24
2.9	48	none	11	23
3.9	none	53	50	94
3.3	none	53	56	106
2.1	none	53	50	94
2.2	none	53	50	94
5.0	none	53	39	74 ^f
3.9	none	53	40	75 ^f
3.6	47	53	64	23 ^g
2.2	47	53	64	23 ^g
3.0	47	53	61	17 ^g

- a. The amount of calcium carbonate was determined by weighing. The calcium carbonate aerosol was added immediately following the collection of the sulfuric acid aerosol and the total sampling time was approximately 20 to 30 min.
- b. The amount of sulfuric acid aerosol added to each filter was determined by analysis of a parallel filter exposed only to sulfuric acid aerosol.
- c. Analytical spikes of sulfuric acid were added to some of the filter extracts.
- d. All analyses for sulfuric acid were conducted with the benzaldehyde extraction technique and the Ba-Thorin microtitration.
- e. nd = not detected
- f. These results are for sulfuric acid spikes added to benzaldehyde extracts containing suspended calcium carbonate particulate.
- g. These recoveries are calculated for the sulfuric acid aerosol assuming the spikes were recovered with 100% efficiency.

TABLE 16. EFFECT OF PREDEPOSITED CALCIUM CARBONATE UPON
SULFURIC ACID AEROSOL COLLECTED ON MITEX LS FILTERS

CaCO ₃ aerosol added, mg ^a	H ₂ SO ₄ aerosol added, µg ^b	H ₂ SO ₄ spike added, µg ^c	H ₂ SO ₄ found, µg ^d	Recovery, %
3.6	56	none	6	11
5.2	56	none	8	14
5.0	57	none	15	26
2.5	none	53	36	68 ^e
2.4	none	53	38	72 ^e
none	none	53	46	87 ^f
none	none	53	47	89 ^f

- The amount of calcium carbonate was determined by weighing. The calcium carbonate aerosol was added prior to the collection of sulfuric acid aerosol and the total sampling time was 20 to 30 min.
- The amount of sulfuric acid aerosol added to each filter was determined by analysis of a parallel filter exposed only to sulfuric acid aerosol.
- Analytical spikes of sulfuric acid in benzaldehyde were added to some of the filter extracts.
- All analyses for sulfuric acid were conducted with the benzaldehyde extraction technique and the Ba-Thorin microtitration.
- These results are for sulfuric acid spikes added to benzaldehyde extracts containing suspended calcium carbonate particulate.
- These data are typical values for the recovery of sulfuric acid from standard solutions in benzaldehyde.

exposures of sulfuric acid aerosol to predeposited calcium carbonate. The data in both tables demonstrate the favorable recovery of analytical spikes of sulfuric acid in the workup of the samples; also, matrix effects are shown to be negligible. However, it is evident from these results that a marked loss of sulfuric acid occurred on the filters in the presence of collected calcium carbonate aerosol. Whether the sulfuric acid aerosol was added before or after the collection of calcium carbonate aerosol, losses of sulfuric acid generally in excess of 75% were observed (i.e.,

recoveries were typically less than 25%). It can be speculated that the losses of sulfuric acid were the result of reaction of the acid with calcium carbonate to form calcium sulfate. Because of the possibility of formation of this product, experiments were conducted in which it was demonstrated that calcium sulfate was not extracted from filters with benzaldehyde and therefore, did not interfere with the quantitation of sulfuric acid. These results are in general agreement with those described previously in which the less specific bromophenol blue method for the determination of sulfuric acid was used. Both investigations show that a potential problem exists in sampling sulfuric acid aerosol simultaneously with an alkaline reactant such as calcium carbonate.

Ferric Oxide--

The experiments to investigate the influence of particulate ferric oxide upon the stability of collected sulfuric acid aerosol were performed in a manner comparable to those described for particulate calcium carbonate. The results are presented in Table 17. These data also point out the favorable recovery of analytical spikes and the apparent freedom from matrix effects in the determination of sulfuric acid in the presence of ferric oxide particulate. Upon analysis of filters exposed to sulfuric acid aerosol following collection of ferric oxide particulate, insignificant losses of sulfuric acid were observed. Indeed, approximately 95% of the added sulfuric acid was found to remain unchanged on the filters loaded with ferric oxide particulate. This result concurs roughly with data obtained on ferric oxide interference with the less specific bromophenol blue method. The results of both of these investigations indicate that ferric oxide particulate does not pose a severe interference in the collection and quantitation of sulfuric acid aerosol.

Fly Ash--

The experiments to investigate the influence of fly ash upon the stability of sulfuric acid collected on Mitex filters from an aerosol were performed in a manner comparable to the experiments described for the particulates ferric oxide and calcium carbonate. In the present experiments, fly ash was deposited on Mitex filters from an aerosol before the collection of sulfuric acid. The sample of fly ash employed in these experiments was obtained from the electrostatic precipitator of a coal-fired power plant and was reported to contain 0.5% of water-soluble sulfate.

The results of the study of fly ash interference are presented in Table 18. These data show that no contribution from residual sulfate in the fly ash was detected in the analyses with the benzaldehyde extraction technique. Also, spikes of sulfuric acid in benzaldehyde that were added to filter extracts in the presence of suspended fly ash particulate were recovered with

TABLE 17. EFFECT OF PREDEPOSITED FERRIC OXIDE
UPON SULFURIC ACID AEROSOL COLLECTED
ON MITEX LS FILTERS

Fe ₂ O ₃ aerosol added, mg ^a	H ₂ SO ₄ aerosol added, µg ^b	H ₂ SO ₄ spike added, µg ^c	H ₂ SO ₄ found, µg ^d	Recovery, %
0.3	none	none	nd	-
0.5	none	none	nd	-
0.3	52	none	52	100
0.4	45	none	43	96
0.2	43	none	39	91
0.3	none	43	36	84 ^e
0.5	none	43	34	79 ^e
none	none	43	39	91
none	none	43	35	81

^a The amount of ferric oxide was determined by weighing. The ferric oxide aerosol was added prior to the collection of sulfuric acid aerosol and the total sampling time was 20 to 30 min.

^b The amount of sulfuric acid aerosol added to each filter was determined by analysis of a parallel filter exposed only to sulfuric acid aerosol.

^c Analytical spikes of sulfuric acid in benzaldehyde were added to some of the filter extracts.

^d All analyses for sulfuric acid were conducted with the benzaldehyde extraction technique and the barium Ba-Thorin microtitration.

^e These results are for sulfuric acid spikes added to benzaldehyde extracts containing suspended ferric oxide particulate.

TABLE 18. EFFECT OF PREDEPOSITED FLY ASH UPON SULFURIC ACID COLLECTED ON MITEX LS FILTERS

Fly ash added, mg ^a	H ₂ SO ₄ added, µg ^b	H ₂ SO ₄ spike, µg ^c	H ₂ SO ₄ found, µg	Recovery, %
4.3	none	none	nd ^d	-
3.4	none	none	nd	-
1.5	none	43	36	84
1.5	none	43	38	88
1.8	40	none	32	80
1.5	38	none	28	74
2.8	38	none	31	82

^a The amount of fly ash was determined by weighing. The fly ash was collected prior to the collection of sulfuric acid and the total sampling time was 20 to 30 min.

^b The amount of sulfuric acid added to each filter was determined by analysis of a parallel filter exposed only to the sulfuric acid aerosol.

^c Analytical spikes of sulfuric acid in benzaldehyde were added to some of the filter extracts that contained suspended fly ash particulate.

^d nd = not detected.

efficiencies of 84 and 88%. (Analyses of standard solutions of sulfuric acid in benzaldehyde generally result in recoveries of 80 to 90%.) The high recovery of sulfuric acid spikes indicated that sulfuric acid was not lost in the analytical work-up of the filter samples.

Upon addition of sulfuric acid to filters preloaded with fly ash it was found on analysis that essentially all of the sulfuric acid was recovered. The recovery of sulfuric acid from three filters averaged 79% and it appeared that this particular fly ash sample caused no substantial degradation of the collected sulfuric acid.

Although this appears to be a significant result for fly ash, we cannot at this time predict whether or not this would be the general result for variety of diverse fly ash samples. An additional uncertainty in these experiments with fly ash concerns the possibility of benzaldehyde extraction of bisulfates or sulfates resulting from reaction of the fly ash with the added sulfuric acid aerosol. In several studies concerning the potential interferences posed by pure reagents such as calcium carbonate and ammonia, the possibility of nonselective extraction of the corresponding bisulfates or sulfate was investigated with known spikes of the authentic materials on filter disks. However, the complexity of fly ash precludes the measurement of the extractability of all of the possible sulfate and bisulfate compounds that could be formed on reaction of the fly ash with sulfuric acid. On the other hand, an analytical result which indicates that a loss of sulfuric acid occurred on a filter in the presence of a predeposited interferent (and not in the analytical workup) not only identifies an active interference to collection of sulfuric acid but also demonstrates that coextraction of bisulfates and sulfates into benzaldehyde did not take place in the analysis for residual sulfuric acid. Such a result is demonstrated by the data from the study of the effect of ambient particulate material on sulfuric acid.

Soot--

Experiments to study the influence of soot (amorphous carbon) on the stability of collected sulfuric acid were performed in a manner comparable to other experiments with particulate interferents. The soot was predeposited onto tared filters from a fuel-rich acetylene-air flame and, after collection of sulfuric acid, the filters were analyzed with the usual benzaldehyde extraction technique. The results of these experiments are given in Table 19. These data also show no sulfate contribution from the soot and demonstrate adequate recovery of spikes (79 and 81%) in the presence of the soot. The recovery of sulfuric acid collected on the soot-loaded filters averaged about 81%. Therefore, under these experimental conditions, soot was not found to be detrimental to the stability of sulfuric acid collected on the preloaded filters.

Silicate Dust--

Efforts to determine the effect of finely ground concrete on the determination of sulfuric acid predeposited on a filter were not successful when the analysis was attempted by the benzaldehyde extraction method. The strong alkalinity of the concrete dust appeared to interfere in the analysis. Another experiment was run with a different silicate dust, a fire clay from Golden, Colorado. The results in Table 20 indicate some apparent loss of acid occurred, particularly with the larger amounts of the clay.

TABLE 19. EFFECT OF PREDEPOSITED SOOT UPON SULFURIC ACID
COLLECTED ON MITEX LS FILTERS

Soot added, mg ^a	H ₂ SO ₄ added, µg ^b	H ₂ SO ₄ spike, µg ^c	H ₂ SO ₄ found, µg	Recovery, %
1.2	none	none	nd ^d	-
1.1	none	none	nd	-
0.9	none	58	46	79
0.9	none	58	47	81
0.9	40	none	33	83
0.9	35	none	28	81
0.7	34	none	27	80

^a The amount of soot was determined by weighing. The soot was collected from an aerosol prior to the collection of sulfuric acid and the total sampling time was 20 to 30 min.

^b The amount of sulfuric acid added to each filter was determined by analysis of a parallel filter exposed only to the sulfuric acid aerosol.

^c Analytical spikes of sulfuric acid in benzaldehyde were added to some of the filter extracts that contained suspended soot particulate.

^d nd = not detected.

TABLE 20. EFFECT OF PREDEPOSITED CLAY UPON SULFURIC ACID COLLECTED ON MITEX LS FILTERS

Clay added, mg ^a	H ₂ SO ₄ added, μ g ^b	H ₂ SO ₄ spike, μ g ^c	H ₂ SO ₄ found, μ g	Recovery, %
1.8	none	none	<5	-
2.6	none	none	<5	-
1.2	none	62	55	89
2.9	none	62	50	81
0.9	52	none	46	88
1.2	67	none	51	76
2.2	43	none	23	53

^a The amount of clay was determined by weighing prior to the collection of sulfuric acid aerosol.

^b The amount of sulfuric acid added was determined by analysis of a parallel filter exposed only to the sulfuric acid aerosol.

^c Analytical spikes of sulfuric acid in benzaldehyde were added to some of the filter extracts that contained suspended clay.

Analyses with a Flame Photometric Detector

Ambient Particulate Material--

Sample heated to 200°C--Tracings of flame photometric responses of sample disks cut from a filter loaded with 0.5 mg of ambient particulate matter, a reference filter loaded with about 50 μ g of sulfuric acid deposited from an aerosol, and a filter loaded with 0.5 mg of ambient particulate matter plus about 50 μ g of sulfuric acid aerosol are shown in Figure 6. These experiments were done under the following conditions: range, 0-500 mV; chart speed, 1 in./min; temperature, 200°C; hold time, 1 min. Sulfuric acid was collected from the output of the laboratory aerosol generator during the simultaneous exposure of a clean filter (reference) and a filter preloaded with ambient particulate matter (sample). The filters were mounted in parallel sampling lines and samples were collected for 20 min at the rate of 6 l/min. Equal amounts of sulfuric acid were thus deposited on each of the filters. The ambient particulate matter was collected at a sampling station located in the vicinity of the Institute. This station was about 5 m from a busy street. The total volume of air sampled was about 10 m³. The filters were stored in a desiccator until they could be analyzed.

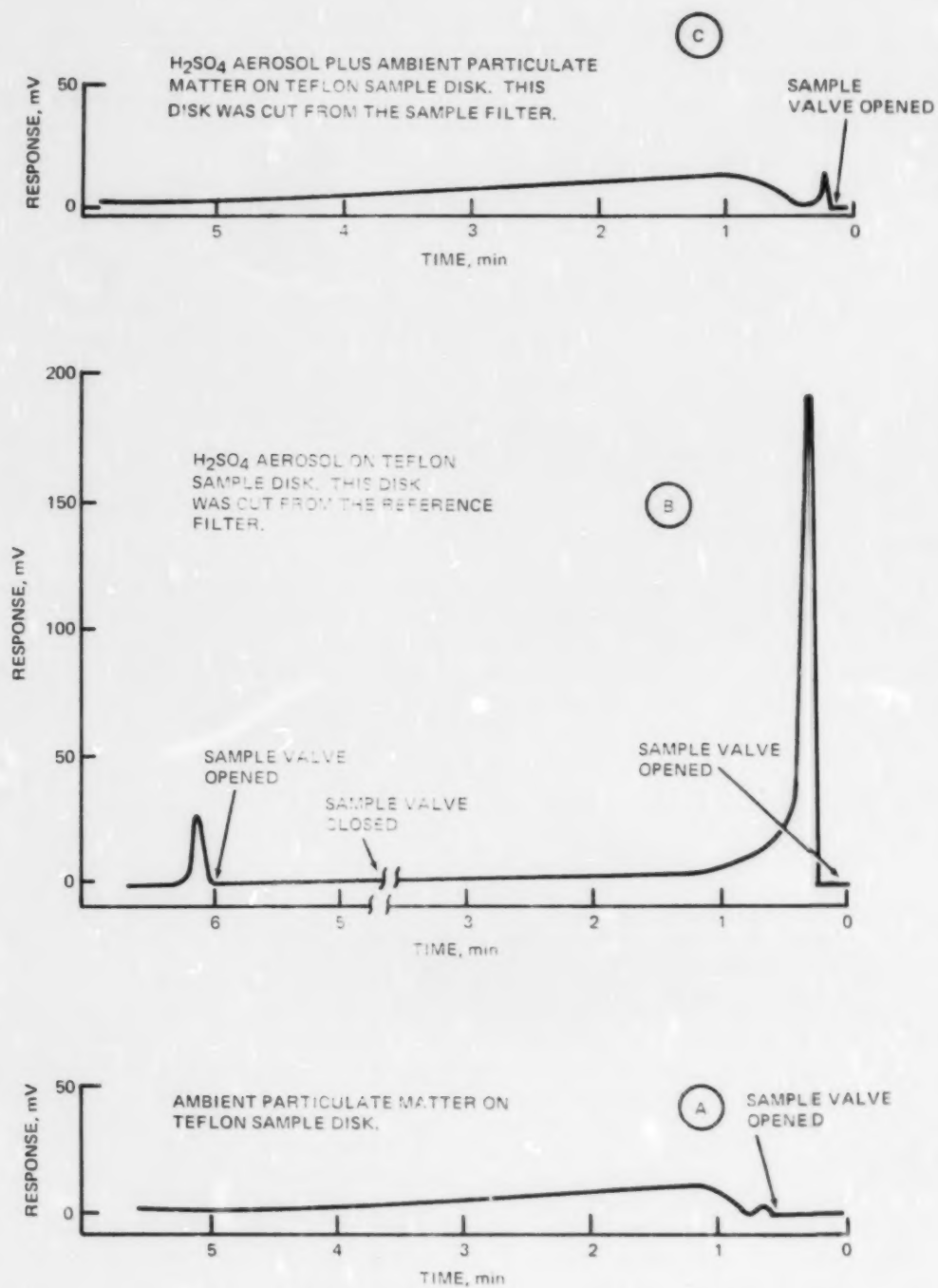


Figure 6. Effect of Predeposited Ambient Particulate Matter on Flame Photometric Detection of Sulfuric Acid. Temperature, $200^{\circ}C$.

Figure 6A shows the flame photometric response to ambient particulate matter alone. The initial peak may or may not be due to ambient sulfuric acid. The more gradual response followed by the very slow decay of the signal is assumed to be due to sulfur compounds that are more difficult to volatilize than sulfuric acid or that are slowly liberated at the elevated temperature. The flame photometric response to sulfuric acid alone is shown in Figure 6B. This response is similar to those obtained with standard samples of sulfuric acid shown in Figure 3. The total amount of sulfuric acid on the reference filter, calculated from the flame photometric response, was 54 μg . This is about the amount expected based on the operating parameters of the sulfuric acid aerosol generator. Figure 6C shows the flame photometric response to a disk cut from the sample filter that was loaded with ambient particulate matter and sulfuric acid. There is a marked decrease in the magnitude of the peak that is attributed to sulfuric acid. The gradual increase and slow decay of signal following the initial peak is, again, assumed to be due to difficulty volatilized sulfur compounds. Since the calibration data in Table 3 did not cover the range for amounts of sulfuric acid significantly less than 1 μg , it is not feasible to estimate the sulfuric acid concentration represented by this peak.

Sample heated to 150°C--The curves in Figure 7 show the flame photometric responses to samples of sulfuric acid, ambient particulate matter, and ambient particulate matter plus sulfuric acid at 150°C. The load of ambient particulate matter on each of the two preloaded filters was 0.5 mg. The nominal amount of sulfuric acid on the reference and sample filters was 50 μg . The transfer line and the detector block remained at 200°C. Unlike the experiments with the sample block at 200°C (Figure 6), a 2-min hold time was used in the experiments at 150°C. In other respects--methods of sample collection, air and hydrogen flow rates, and recording conditions--the experiments at 150°C were identical to those at 200°C. No attempt was made to quantitate the results of the experiments at 150°C; however, the curves do show that the magnitude of the responses for standard samples deposited from a syringe and for filter samples deposited from an aerosol were much smaller at 150°C than at 200°C. Figures 7B and 7D are responses for samples of ambient particulate matter and ambient particulate matter plus sulfuric acid. The curves are almost identical, illustrating the difficulty of recovering sulfuric acid at 150°C from filters containing ambient particulate matter.

Effect of hold time--Figure 8 illustrates the effect of hold time at 200°C on the response to samples of ambient particulate matter plus sulfuric acid deposited from an aerosol. These samples were 7.3-mm diameter disks cut from a Mitex LS filter that was preloaded with 0.5 mg of ambient particulate matter and then loaded with about 50 μg of sulfuric acid. The gas flows and recording conditions were the same as those previously described. The curves show that the magnitude of the initial peak increased

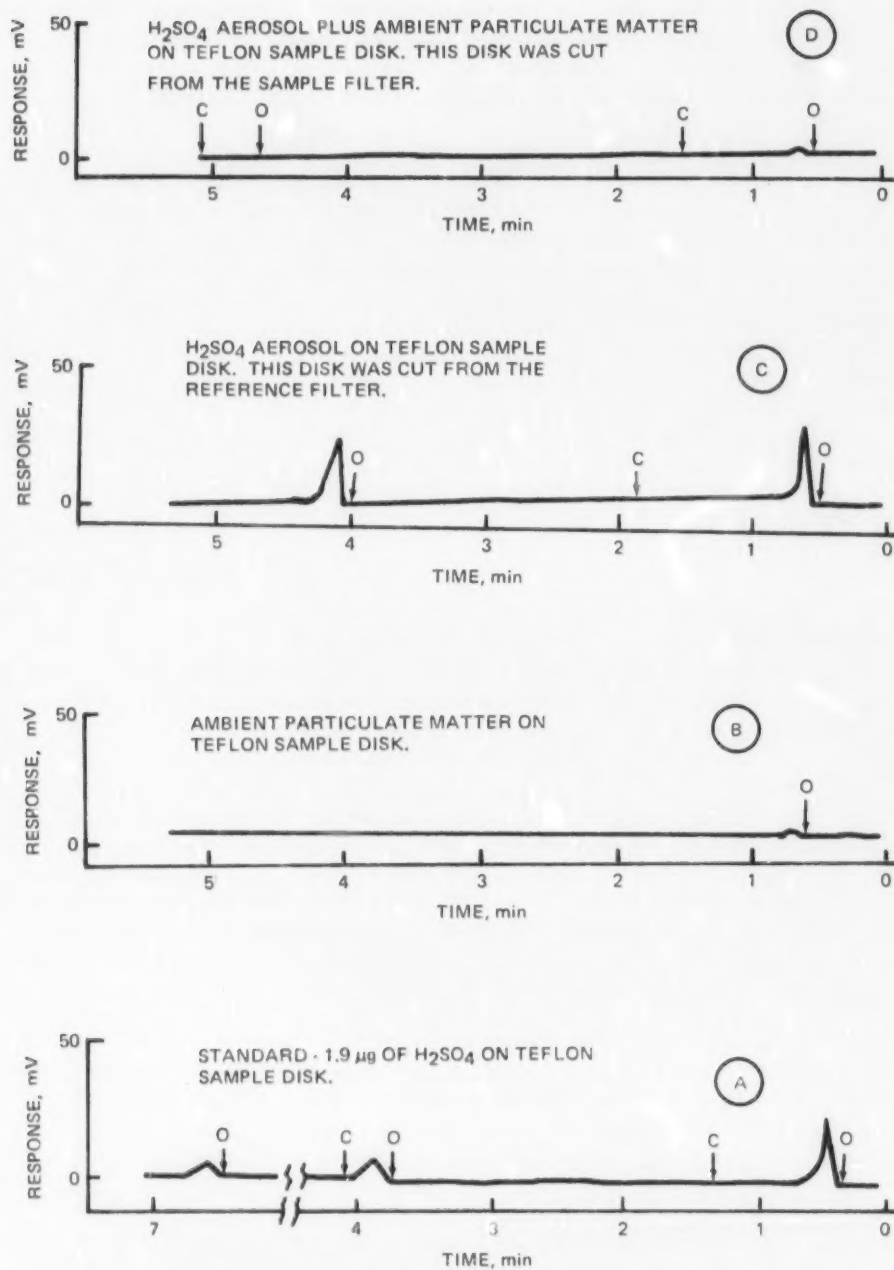


Figure 7. Effect of Predeposited Ambient Particulate Matter on Flame Photometric Detection of Sulfuric Acid. Temperature, 150°C .
 O = Sample Valve Opened; C = Sample Valve Closed

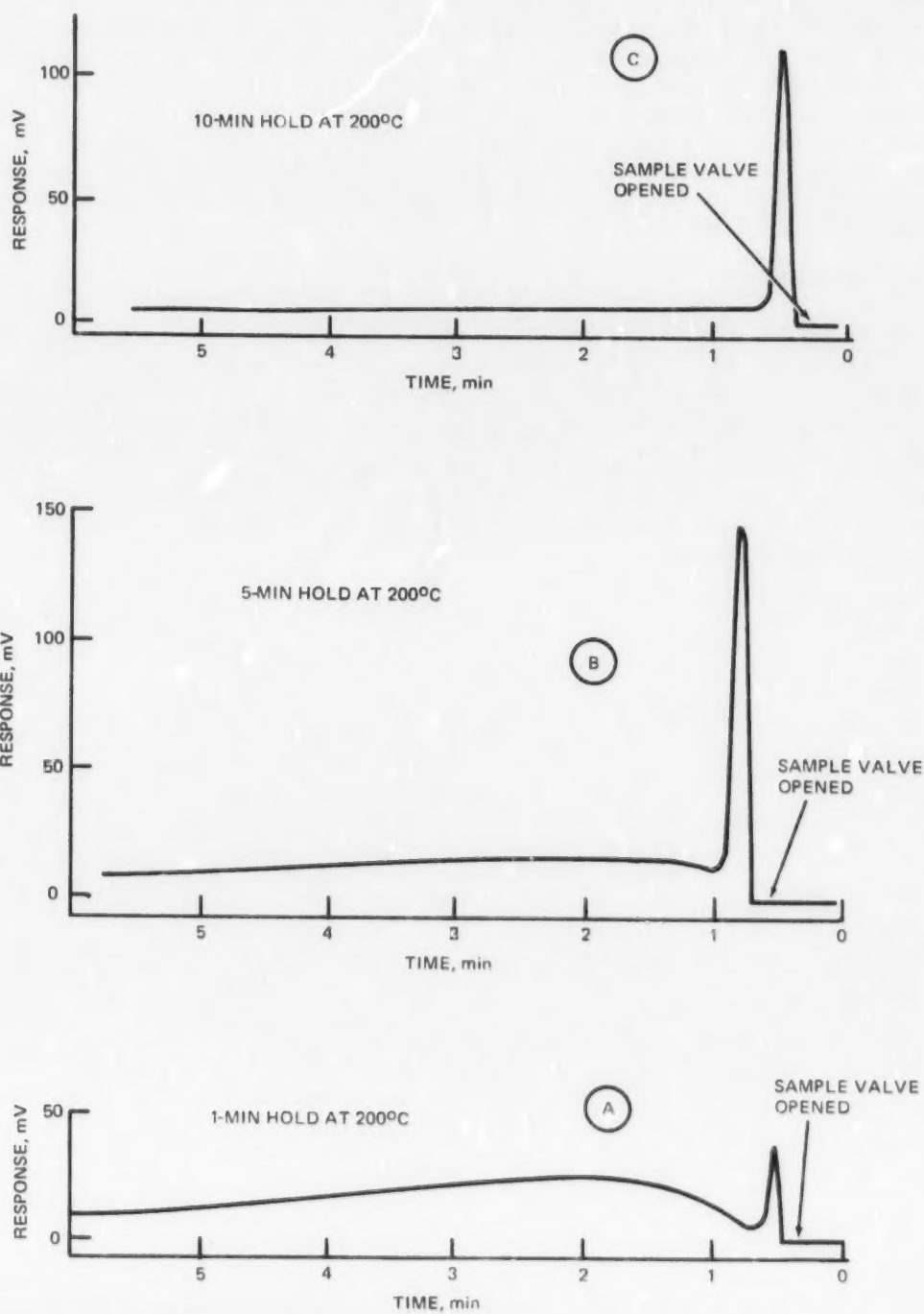


Figure 8. Effect of Hold Time on Flame Photometric Response. Teflon Sample Disks Loaded with Sulfuric Acid and Ambient Particulate Matter

and the broad band following the initial peak decreased as the hold time was increased from 1 min to 5 min (Figures 8A and 8B). This observation suggested that difficultly volatilized or slowly decomposing sulfur compounds may contribute to the initial peak if the hold time is too long at 200°C. Although there was not a drastic increase in the size of the peak (area) between the 5-min hold and the 10-min hold at 200°C, the "hump" in the curve disappeared (Figures 8B and 8C).

Calcium Carbonate--

The results obtained with the flame photometric measurements agreed with similar experiments conducted with the benzaldehyde extraction technique. That is, the sulfuric acid collected on a filter was lost upon exposure to particulate calcium carbonate whether the acid was collected before or after the deposition of the calcium carbonate. This result is demonstrated in Figures 9, 10, and 11. Figure 9B shows the slight response obtained with calcium carbonate alone, probably due either to an impurity in the calcium carbonate or to residual sulfur in the apparatus.

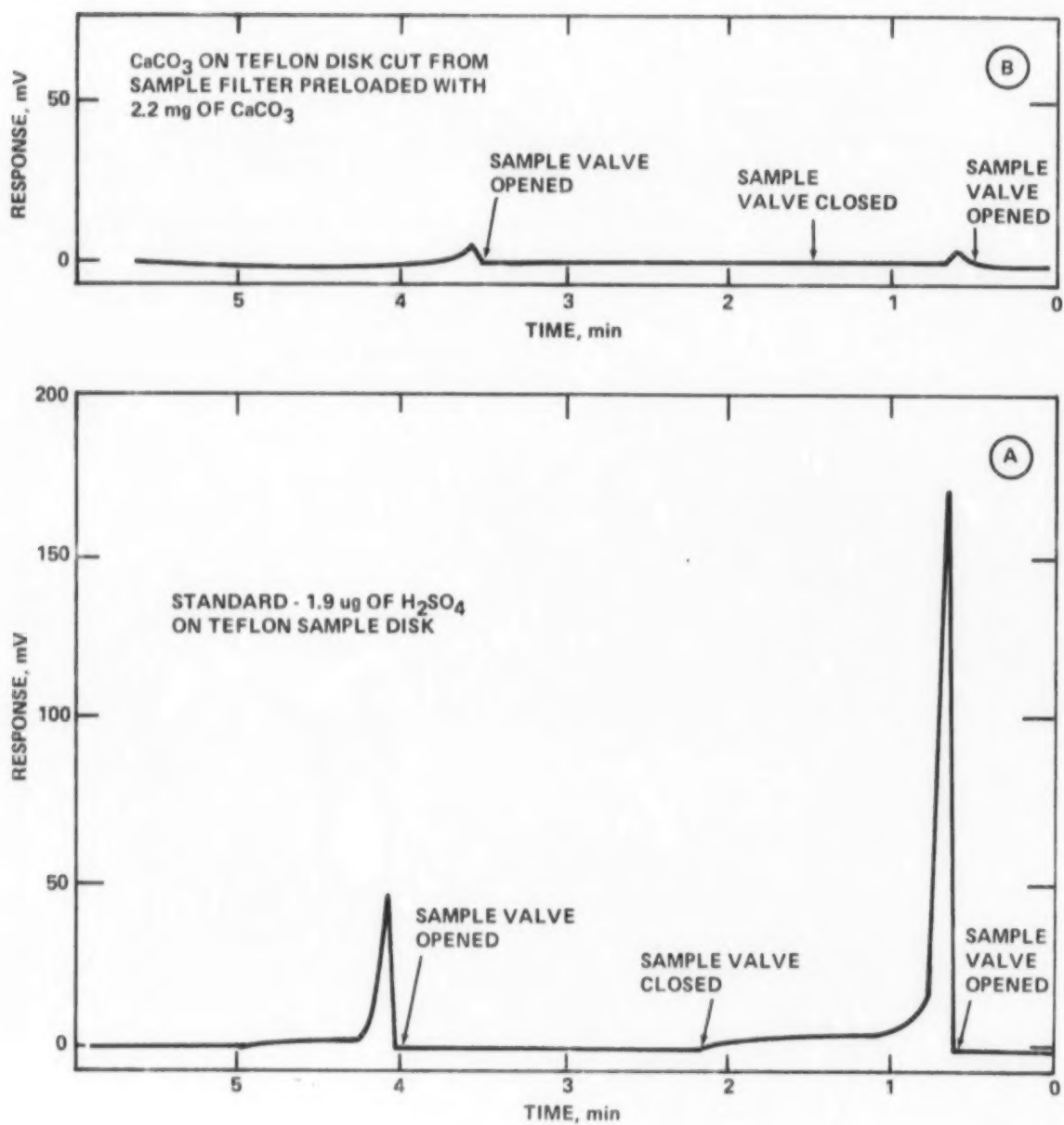


Figure 9. Flame Photometric Response to Sulfuric Acid Alone and to Calcium Carbonate Alone. Temperature, 200°C.

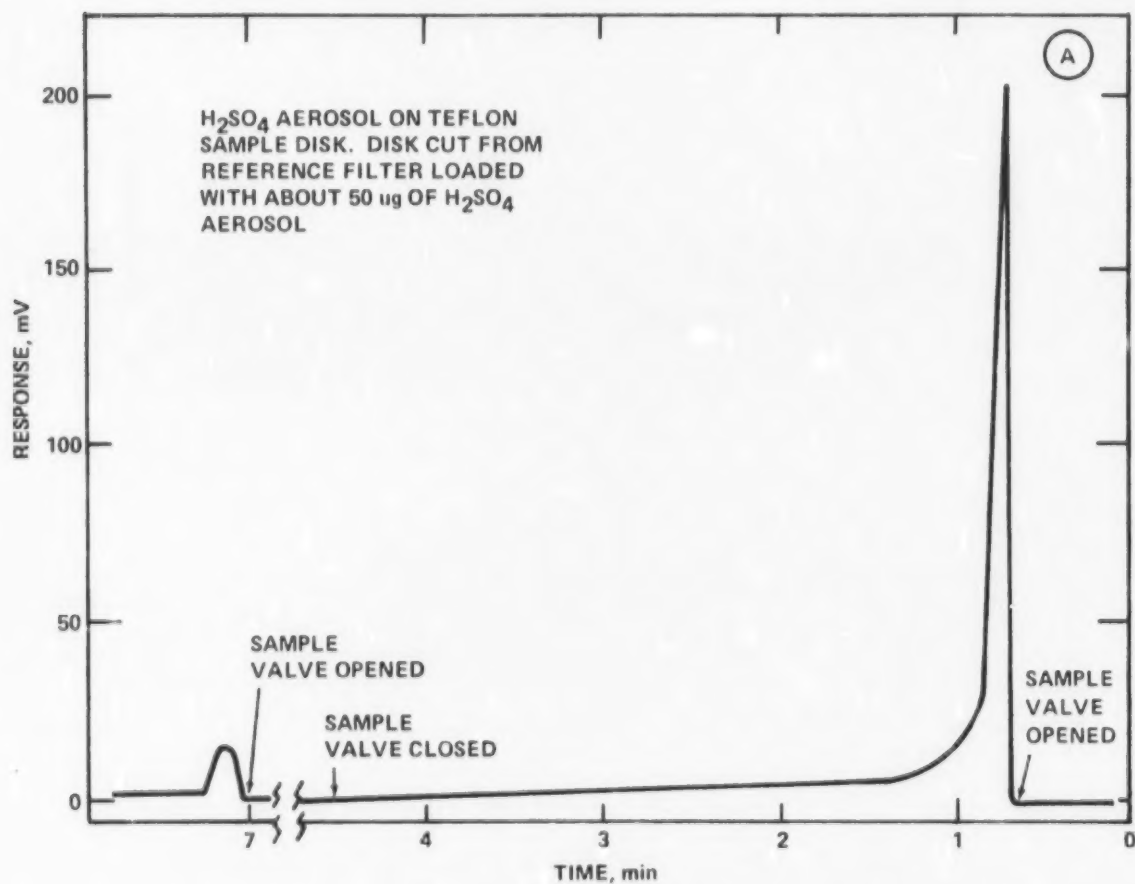
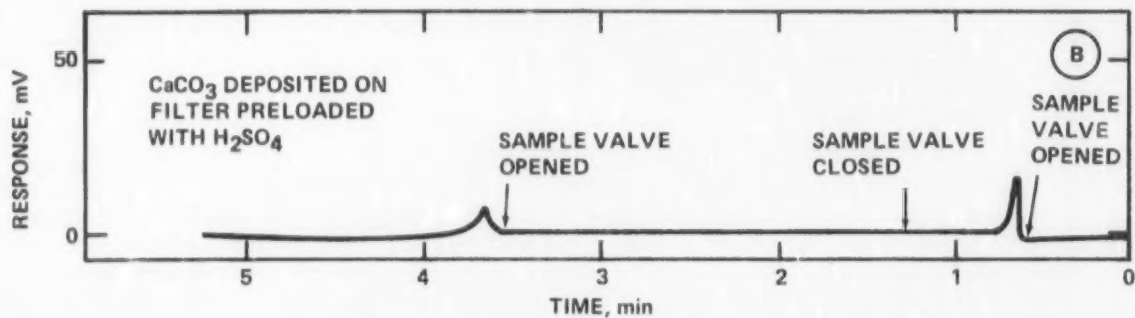


Figure 10. Effect of Calcium Carbonate on Flame Photometric Detection of Predeposited Sulfuric Acid. Temperature, 200°C.

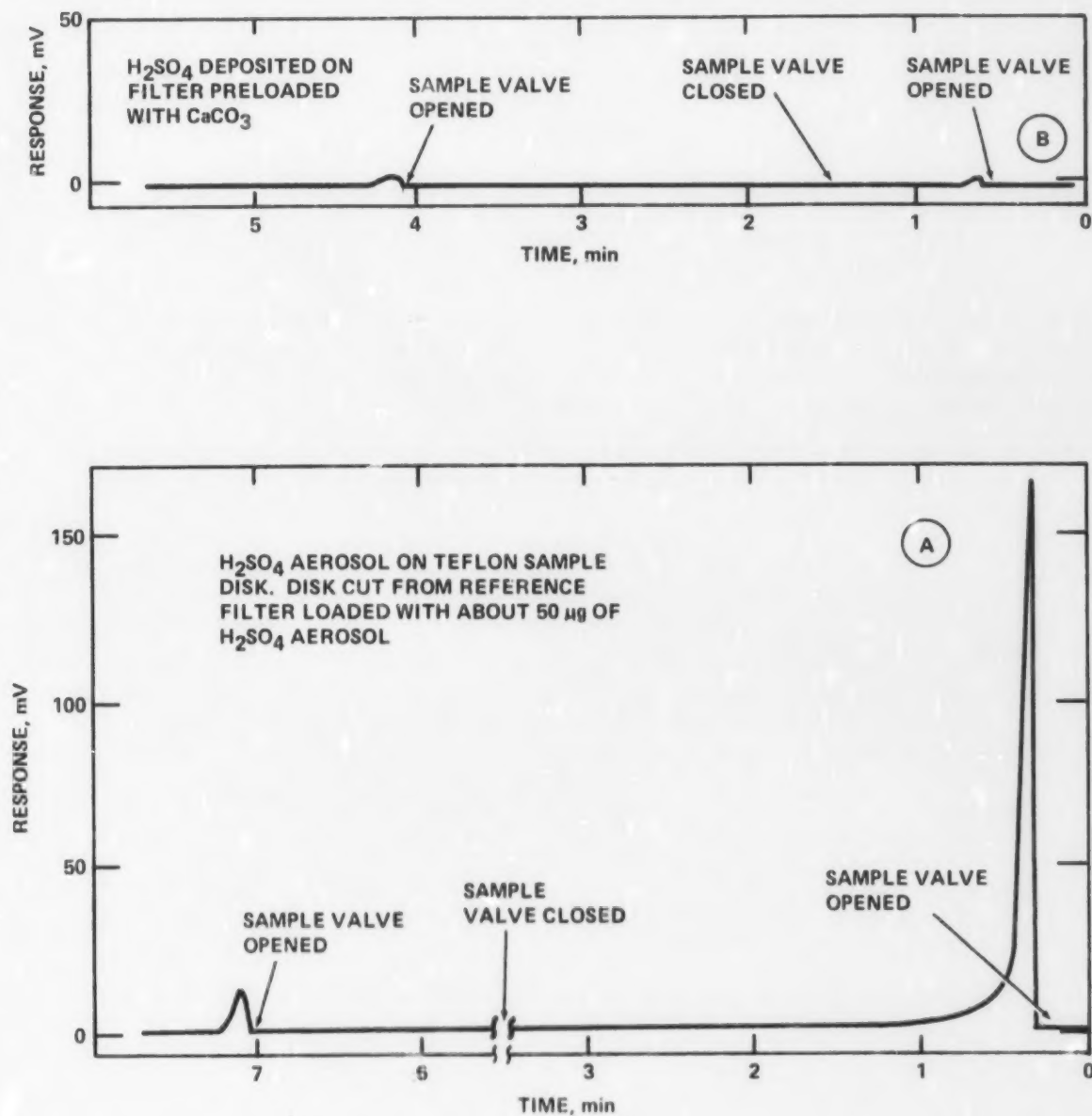


Figure 11. Effect of Predeposited Calcium Carbonate on Flame Photometric Detection of Sulfuric Acid. Temperature, 200°C.

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